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THE CHEMISTRY AND TECHNOLOGY OF HIGH EXPLOSIVES

BY: Ye. Yu. Orlova

English Pages: 752

PART II
Pages 252 through 567

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Part II

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Section 1. Chemistry of the Production of, Properties of, and Applications of the Nitro Derivatives of Benzene

Benzene is a colorless, highly refractive liquid with a characteristic aroma. Its boiling point is 80.1°, melting point 5.58°, specific gravity $d_{4^\circ}^{15^\circ} = 0.8787$, $d_{4^\circ}^{50^\circ} = 0.8454$.

Technical benzene always contains foreign impurities. The major impurities in benzene from coal are sulfur compounds: thiophene (boiling point 84°), which may constitute up to 0.5% of the whole, and traces of carbon disulfide (boiling point 47°).

Thiophene differs from benzene by its capacity vigorously to oxidize nitric acid, and therefore, in the nitration of benzene, additional nitric acid is expended to oxidize the thiophene.

Thiophene and carbon disulfide are usually not present in benzene made from petroleum. However, this benzene does contain a considerable quantity (up to 5%) of gasolines, as well as of unsaturated hydrocarbons.

The following specifications must be met by coal-derived benzene to be used for nitration: specific gravity $d_{4^\circ}^{20^\circ} = 0.875 - 0.880$; boiling point between 79.0 - 80.6°. The degree of purification is determined by the absorption of bromine (the bromine titer must not be more than 0.42 per 100 cc benzene), and by the color due to sulfuric acid (not more than 30% of a standard sample). Moreover,

131 not less than 95% of the benzene by volume should distill within 0.8°. The benzene is tested for the presence of these impurities in a manner similar to the testing of the toluene, as described in the section "Trinitrotoluene".

Benzene is difficultly soluble in water: 100 cc water dissolve 0.082 cc benzene at 20°. Benzene will mix with alcohol, ether, acetone, carbon disulfide,

and ligroin,
in any ratios. It is a solvent for fats, oils, rubber, nitrocellulose, etc., and burns with a very smoky fire.

Benzene is toxic, and safety rules must be strictly adhered to in working with it.

Benzene is transported in iron tank cars. Inasmuch as it has a high freezing point, it is necessary to thaw frozen benzene in winter. This is usually done in thawing sheds, in which the temperature of 40 - 30°C is maintained, and in which the benzene thaws out in 24 - 30 hrs. Other methods of thawing frozen benzene are also employed.

Mononitrobenzene is formed upon nitration of benzene by nitric acid or mixed acid, in accordance with the equation

$$C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O.$$

Mononitrobenzene is a yellow liquid smelling of bitter almonds. It boils at 210.6°, freezes at 5.7°, and its specific gravity is $d_4^{15^\circ} = 1.204$.

Mononitrobenzene is readily distillable by steam. Its solubility in sulfuric acid and mixed acid at 43° (Bibl.81) is presented in Table 33.

Table 33

a)	b)	c)	d)
50	0,02	40—50	about 0,015
60	0,03	60	about 0,02
70	0,04	—	—

a) Strength of H_2SO_4, %; b) Solubility of mononitrobenzene, %; c) Strength of H_2SO_4, containing 0.2% HNO_3, %;

Mononitrobenzene dissolves very slightly in water, but well in ether, alcohol, benzene, and strong nitric acid. It is itself a solvent for many organic substances, including nitrocellulose, with which it forms a gelatinlike substance. In its chemical properties, it is typical nitrocompound, and yields aniline upon reduction. It dissolves in sulfuric acid, but if undissolved nitrobenzene remains, it can be extracted by anhydrous sulfuric acid out of the acid layer, yielding a compound of the following composition $C_6H_5NO_2 \cdot H_2SO_4$ (Bibl.82).

In the liquid form, mononitrobenzene does not have explosive properties. However, in the gaseous form and in a vessel heated to high temperature under pressure, it is capable of decomposing with great force (Bibl.83).

Mononitrobenzene is widely used as an intermediate product in the aniline dye industry for the production of aniline. A small amount thereof goes to the making of chlorate explosives, in which it serves as fuel and phlegmatizer.

Dinitrobenzene. Nitration of mononitrobenzene by mixed acid yields technical dinitrobenzene:

$$C_6H_5(NO_2) + HNO_3 \rightarrow C_6H_4(NO_2)_2 + H_2O.$$

The nitration velocity of mononitrobenzene under homogeneous conditions rises, as was demonstrated by Martinsen (Bibl.84), with increase in sulfuric acid strength to 89.1%, and thereafter it falls. Hetherington and Mason (Bibl.85) have investigated this reaction under heterogeneous conditions and determined that the nitration reaction proceeds only in the mineral phase.

Mononitrobenzene may be nitrated to meta-dinitrobenzene by nitric acid in the presence of boron fluoride (Bibl.86) with a yield of up to 90%. Nitration of mononitrobenzene by sodium nitrate with excess strong sulfuric acid yields the same good yield of dinitrobenzene as when fuming nitric acid is employed.

Dinitrobenzene may be produced by nitration of benzene, and in a single stage (Bibl.87).

Technical dinitrobenzene, obtained by nitration of mixed acid with f.n.a. = 86% at 75 - 80°, consists of three isomers and has the following percentage composition (Bibl.88, 89):

Meta-dinitrobenzene	90 - 91
Ortho-dinitrobenzene	8 - 9
Para-dinitrobenzene	1 - 2

The freezing point of technical dinitrobenzene is 81°.

The ortho- and para-dinitrobenzene isomers constitute an undesirable impurity in meta-dinitrobenzene. The yield of the meta-dinitrobenzene isomer depends upon the nitration temperature (Bibl.88, 90) which is evident from Table 34.

Table 34

a)	b)	c)		
		d)	e)	f)
—17 to —10	86,9	95,1	2,5	2,4
—5 to +5	86,8	94,7	3,5	1,8
25—29	85,0	92,6	5,0	2,4
65—69	83,0	89,3	7,7	3,0
90—100	80,0	87,0	7,8	1,2
124—129	79,9	85,7	13,9	0,4

a) Nitration temperature °C; b) Freezing point °C; c) Percentage composition of dinitrobenzene obtained; d) Meta-; e) Ortho-; f) Para-

132 Tables 35 - 37 present certain physical-chemical constants and properties of the isomers of dinitrobenzene, from which it follows that the meta-isomer, which is the chief product of nitration, is more soluble than the other two.

Table 35

Product	Melting Point, °C	Boiling Point, °C
Meta-dinitrobenzene	89,7	302
Ortho-dinitrobenzene	116,5	319
Para-dinitrobenzene	172,1	309

Table 36

a)	b)					c)
	20	90	120	140	160	
meta-	1,577	1,3644	1,3349	1,3149	1,2057	0,02528
ortho-	1,59	—	1,3119	1,2915	1,1737	—
para-	1,625	—	—	—	—	—

a) Dinitrobenzene isomers; b) Specific gravity at temperature, °C; c) Viscosity at 90°, g/cm/sec

13

Table 37

a)	b)	c)		
		meta-	ortho-	para-
d)	20,5	6,75	3,3	0,69
e)	20,5	3,5	1,9	0,40
f)	20,0	2,4	1,09	0,30
g)	17,6	1,35	0,24	0,14
h)	17,6	32,4	27,1	1,82
i)	18,2	39,45	5,68	2,56
j)	18,2	36,27	12,96	3,56
k)	16,5	30,66	3,63	2,36
l)	16,5	1,18	0,14	0,12
m)	20,0	0,02	0,01	0,01
m)	100,0	0,32	0,30	0,30

a) Solvent; b) Temperature, °C; c) Parts of dinitrobenzene dissolving in 100 parts of solvent; d) Methyl alcohol; e) Ethyl alcohol; f) Propyl alcohol; g) Carbondisulfide; h) Chloroform; i) Benzene; j) Ethyl acetate; k) Toluene; l) Carbontetrachloride; m) Water

133 The solubility of meta-dinitrobenzene in 100 parts of sulfuric acid XX of various strengths is presented in Table 38 (Bibl.91).

Table 38

a)	b)		
	70	80	90
0	0,60	1,4	7,15
10	0,65	1,4	7,2
25	0,75	1,7	7,9
40	0,90	1,8	9,0
50	1,00	2,2	10,1
60	1,15	2,7	11,25
70	1,40	3,5	13,40
80	1,85	4,0	16,0
90	2,05	4,8	18,6
100	3,00	6,5	22,3

a) Temperature, °C; b) Percentage solubility of meta-dinitrobenzene in sulfuric acid of various strengths, in %

The comparatively low solubility of meta-dinitrobenzene in sulfuric acid facilitates the separation XX thereof from the spent acid in production.

Dinitrobenzene is a poisonous substance, and the danger of poisoning thereby is increased by its volatility (particularly in steam).

Meta-dinitrobenzene is a neutral substance that does not react with metals.

Upon boiling with caustics, ortho- and para-dinitrobenzene form the corresponding ortho- and para-nitrophenols. Caustic reacts with meta-dinitrobenzene only at elevated XXXX temperature, and the reaction product XXX is apparently a complex chemical compound of unknown composition. With sodium methylate and ethylate, the

134 ortho- and para-dinitrobenzenes form the corresponding nitro anisoles and nitro XXXXXXX phenetoles.

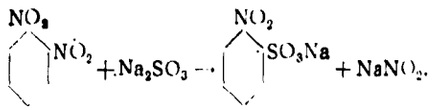
Reaction of sodium methylate and ethylate with XX meta-dinitrobenzene yields XXXXXXX

135 insoluble compounds, brown in color.

Ammonia and methylamine react only with the ortho- and para-dinitrobenzols, yielding the corresponding nitroanilines and nitromethylamines, on the equation

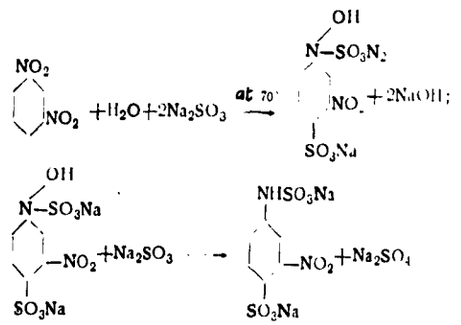
$$C_6H_4(NO_2)_2 + CH_3NH_2 \rightarrow C_6H_4(NO_2)(NHCH_3) + HNO_2.$$

Sodium sulfite exchanges a nitro group for a ~~XX~~ sulfo group in the ortho- and para-dinitrobenzenes, in accordance with the equation

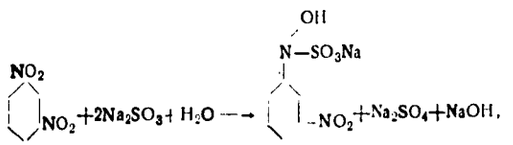


Sodium sulfite reacts with meta-dinitrobenzene only at ~~XX~~ elevated temperature.

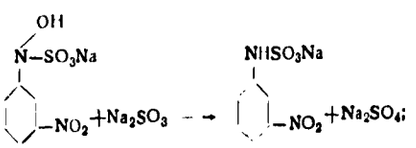
As was demonstrated by O.M.Golosenko, the reaction proceeds in accordance with the following mechanism



There is a side reaction



which, later, upon acidification, results in the formation of unsulfated amines:



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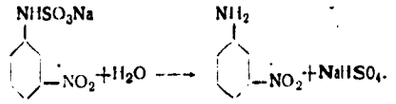
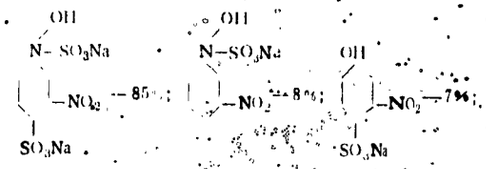
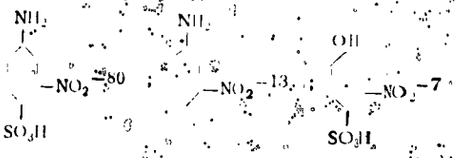


135 The ratios between the compounds formed are:

before acidification



after acidification



Dinitrobenzene is an explosive that is highly stable at elevated temperature and of low sensitivity to mechanical influences (the shock sensitivity is less than that of TNT). Its explosive properties are about 13% weaker than those of TNT (Bibl.35).

The heat of detonation of dinitrobenzene is 820 kcal/kg, the volume of the gaseous explosion products is 635 ltr/kg, the detonation velocity 6100 m/sec, the fugacity is 255 cc, the brisance is 3.4 mm according to Kast, and 10 mm according to Hess.

Dinitrobenzene is poorly detonatable. When cast, it requires a very powerful detonator, but, unpressed, it may be detonated by a cap containing 1.5 gm mercury fulminate, whereas when pressed under a pressure of 290 kg/cm^2 and a density of 1.39 it may be detonated by a cap with 3 gm mercury fulminate, while when pressed under a pressure of 850 kg/cm^2 to a density of 1.44, it cannot be

135 detonated by a 3-gram cap.

Dinitrobenzene with a powerful detonator XX may be employed to fill shells, both as an independent explosive, in the pressed and cast condition; in each case the density of casting may be in the range of 1.48 - 1.5. Most frequently, dinitrobenzene is employed in mixtures with ammonium nitrate, as well as in the form of alloys with other explosives.

A substantial supply of raw materials for the production of dinitrobenzene is available. In this respect, it enjoys a significant advantage over the other XX individual explosives. Therefore, in wartime, the production of dinitrobenzene is expanded XXXX considerably.

A major shortcoming of dinitrobenzene is its toxicity. For this reason, it is produced in peacetime only in quantities required to satisfy the need of the aniline dye industry for XXX production of meta-nitroaniline and meta-phenylenediamine, which are intermediate products for dyes. In wartime, dinitrobenzene is frequently produced in shops that manufacture TNT (when toluene is unavailable), the starting and intermediate products employed in the manufacture of TNT and dinitrobenzene are rather XXXXXX similar in their properties.

During World War I, picric acid xxx was employed in an alloy with dinitrobenzene and a little vaseline, as a phlegmatizer (87% picric acid, 10% dinitrobenzene, and 3% vaseline). In England, this alloy was used to fill armor-piercing shells, and large-caliber shells. In Germany, a mixture of potassium chlorate and dinitrobenzene of the following composition was employed: 56% $KClO_4$; 32% dinitrobenzene; and 12% dinitronaphthalene. When heated, this mixture liquifies, and it is therefore easy to fill shells with it.

136 Alloys of dinitrobenzene and TNT have not found application, as they melt at

low temperatures.

During World War II, dinitrobenzene was employed in a mixture with ammonium nitrate and other explosives in the filling, primarily, of aviation bombs. In Germany, aerial bombs were filled with dinitrobenzene by the so-called piece method: pieces of PTEN, RDX, calcium nitrate, and ammonium nitrate were loaded in, and then melted dinitrobenzene was poured in to fill up.

The use of dinitrobensene to produce ersatz explosives makes it possible to expand the supply of raw materials available.

Trinitrobenzene. The 1,3,5-isomer was first obtained by Hepp (Bibl.16) in 1870 by reacting very strong mixed acid with diritrobenzene at high temperature

$$C_6H_4(NO_2)_2 + HNO_3 \rightarrow C_6H_3(NO_2)_3 + H_2O.$$

1,3,5-Trinitrobenzene is crystallized from alcohol in the form of white platelets of rhombic shape. The freezing point is 123.25°, and the specific gravity 1.69. The density practically attainable by pressing is 1.65.

Table 39 presents data on the solubility of 1,3,5-trinitrobenzene in various solvents (Bibl.92), and Table 40 shows its solubility in sulfuric acid. The Tables show that the best solvent for 1,3,5-trinitrobenzene is pyridine and acetone. The solubility of 1,3,5-trinitrobenzene in sulfuric acid is practically equal to the solubility of meta-dinitrobenzene (see Table 38).

136

Table 39

a)	b)		
	17	50	100
c)	112,60	194,23	—
d)	59,11	160,67	—
e)	29,83	52,40	—
f)	11,86	46,31	—
g)	6,18	25,70	—
h)	6,24	18,42	—
i)	3,78	7,62	—
j)	2,09	4,57	—
k)	1,70	2,72 (at 32°)	—
l)	0,24	0,44 (at 33°)	—
m)	0,03	0,10	0,50

a) Solvent; b) Solubility of trinitrobenzene (in 100 gm solvents), in gm, at temperature in °C; c) Pyridine; d) Acetone; e) Ethylacetate; f) Toluene; g) Benzene; h) Chloroform; i) Methanol; j) Ethanol; k) Ether; l) Carbon disulfide; m) Water

[illegible]

Table 41 presents the melting point of alloys of 1,3,5-trinitrobenzene and meta-dinitrobenzene, which, as is evident from the data presented, first drops, and then increases. This testifies to the existence of a eutectic mixture of 1,3,5-trinitrobenzene and meta-dinitrobenzene. In point of fact, trinitrobenzene-1,3,5 does yield a eutectic mixture with meta-dinitrobenzene, melting at 61.9° (Bibl.87). Some investigators (Bibl.92, 93) regard this to be an unstable modification of 1,3,5-trinitrobenzene. Urbanskiy (Bibl.94) has convincingly demonstrated the absence of dimorphism in 1,3,5-trinitrobenzene.

137

[illegible]

Table 40

a)	b)			
	70	80	90	100
25	0,5	1,05	7,8	21,5
40	0,75	1,75	8,6	24,0
50	0,9	1,9	11,3	26,5
60	1,15	2,3	11,65	28,0
70	1,2	2,95	12,05	32,0
80	1,5	3,75	14,75	34,3
90	2,0	4,15	17,75	37,0
100	2,5	5,90	21,30	42,4

a) Temperature, °C; b) Percentage solubility of trinitrobenzene in sulfuric acid, strength in percentage

Table 41

a)		d)
b)	c)	
100	0	120,3
90	10	109,8
80	20	98,3
70	30	86,2
60	40	74,2
55	45	65,5
50	50	61,9
40	60	65,5
30	70	72,3
20	80	78,2
10	90	84,5
0	100	89,9

a) Composition of alloy of trinitrobenzene and dinitrobenzene; %; [illegible]

b) 1.3,5-trinitrobenzene; c) m-dinitrobenzene; d) Melting point of alloy, °C

1,3,5-Trinitrobenzene is a neutral substance that does not react with metals and oxides thereof. With alcohol solutions of bases, such as TNT, it yields metallic derivatives red in color, having a low detonation point and high sensitivity to mechanical action:

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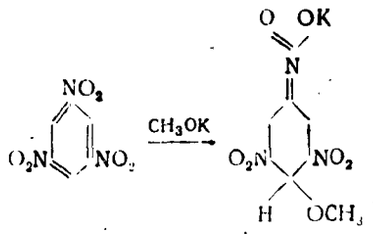
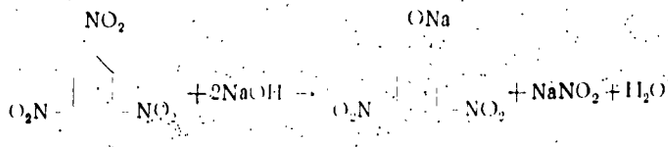
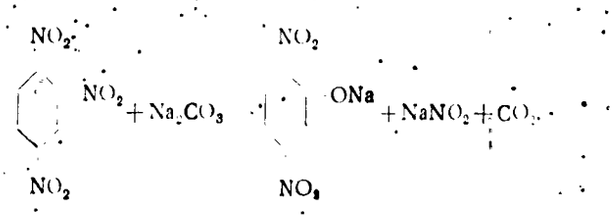


138 Reduction by tin in hydrochloric acid permits the conversion of trinitrobenzene to triaminobenzene. Certain oxidizers (for example, $K_3[Fe(CN)_6]$) transform 1,3,5-trinitrobenzene to picric acid. The dilute solution of caustic soda converts 1,3,5-trinitrobenzene to sodium dinitrophenolates:

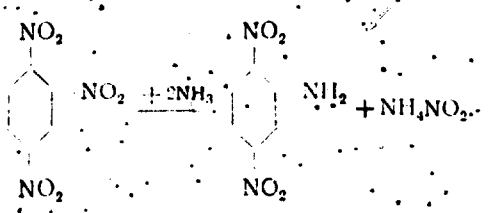


The effect of gaseous ammonia at low temperature XX upon 1,2,3-trinitrobenzene leads to the formation of a reddish brown crystalline mass (with metallic glitter), composition of which reveals a formula of $C_6H_3(NO_2)_3 \cdot 2NH_3$. The presence of moisture , as well as reduction of temperature significantly increase the reaction speed. Like TNT, 1,3,5-trinitrobenzene yields complexes when reacted with various amines, as well as other compounds (Bibl.95,96). With XX phloroglucine, in alkaline solution 1,3,5-trinitrobenzene forms polycyclic compounds (Bibl.97).

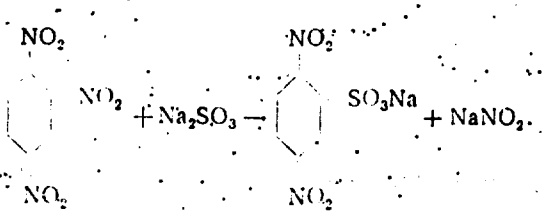
The asymmetrical trinitrobenzenes are more reactive. Thus, substitution of the nitro group by the hydroxyl occurs even under the influence merely of weak soda solutions:



138 When asymmetrical trinitrobenzenes are heated with an aqueous ammonia solution, the nitro group is replaced by the amino group:



When an aqueous sodium sulfite [illegible] solution is reacted with asymmetric [illegible] isomers, sodium salts of dinitrobenzene sulfonic acid result:



Symmetrical 1,3,5-trinitrobenzene forms a compound $C_6H_3(NO_2)_3 \cdot Na_2SO_3$ in caustic or neutral solution. In [illegible] acid solution this compound decomposes [illegible] with the following equation:

$$C_6H_3(NO_2)_3 \cdot Na_2SO_3 + H_2SO_4 \rightarrow C_6H_3(NO_2)_3 + H_2O + Na_2SO_4 + SO_3$$

139 The method employed separates trinitrobenzene from an alloy thereof with dinitrobenzene is based upon this property.

The stability of trinitrobenzene is equal to that of TNT, whereas its shock sensitivity is considerably higher (it explodes upon the dropping of a 2 kg weight from a height of 46 cm, whereas in the case of TNT, the distance required is 100 cm) (Bibl.35). As compared with TNT, the raw materials [illegible] that may be used for production are more extensive, and if a favorable [illegible] solution is found to the problem of production of trinitrobenzene, it could find the same field of application as TNT. An insignificant quantity of trinitrobenzene was employed in World War I in the filling of naval armor-piercing shells.

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139 Table 42 presents the explosive properties of trinitrobenzene.

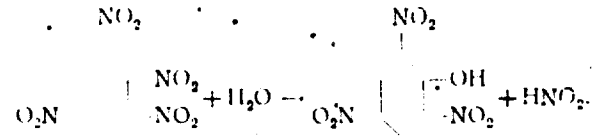
Table 42

Characteristic	Trinitrobenzene
Volume of gaseous explosion products, in ltr/kg	711
Heat of explosion, kcal/kg	1104
Speed of detonation, m/sec	7300
Brisance, due to Kast, mm	4.7
Fugacity, in cc	325

Tetranitrobenzene (Bibl.98) - the 1,2,3,5-isomer - is a crystalline, bright yellow substance, having a melting point of 129 - 130°. It fuses without decomposition in the fused state, and will not decompose in a 6-hour period.

Liquids containing oxygen in their molecules (alcohol, acetone, ether, etc.) will dissolve it. In hydrocarbons and their halide derivatives, 1,2,3,5-tetranitrobenzene dissolves to a sufficient degree (particularly when heated), and is capable of being recrystallized therefrom.

In water, 1,2,3,5-tetranitrobenzene virtually undergoes no dissolution at all, but when it is allowed to stand in a vessel with water, the latter acquires a yellow coloration even within half an hour. The color is due to the reaction of 1,2,3,5-tetranitrobenzene with water, resulting in the formation of picric acid:



The reaction speed increases with increase in temperature, and boiling water completely converts 1,2,3,5-tetranitrobenzene to picric acid within a few minutes. However, storage of the product in the air results in virtually no decomposition,

151 D. Trinitroxylene and Other Nitro Derivatives of Xylene

Trinitroxylene $C_6H(CH_3)_2(NO_2)_3$ (or xylyl) is a product of the nitration of an aromatic hydrocarbon by xylene. Trinitroxylene was first obtained in 1879 by Fittig.

As a consequence of its weak explosive properties, as well as of the comparatively small supply of raw materials for making it (considerably less xylene than toluene is found in the distillation products of coal and petroleum), xylyl has considerably less significance as an explosive than does TNT. Xylyl was widely employed in the First World War, but was used to an only insignificant degree during the Second World War. During the First World War, it was produced in France, the USA, and Russia.

In peacetime, xylyl is employed as a component of ammonium nitrate explosives containing 88% ammonium nitrate and 12% xylyl.

In Russia, the production of xylyl was undertaken on the initiative of prof. A.A.Solonina, who developed a method of producing it by nitration of coal light-fraction resin xylenes by mixed acid. The production of xylyl was undertaken simultaneously at three plants: the Okhta, Krotte, and Shterov. Xylyl was employed in a mixture with ammonium nitrate to fill hand grenades and mines. Later, a mixture of xylyl with TNT and ammonium nitrate was employed to fill shells.

Section 1. Chemistry of Production, Properties, and Applications of Nitro Derivatives of Xylene

Xylene $C_6H_4(CH_3)_2$ (or dimethylbenzene) exists in three isomeric forms: ortho-, meta-, and para-, in addition to which ethyl benzene ($C_6H_5C_2H_5$) is isomeric therewith. The basic physical properties of these aromatic hydrocarbons are presented in Tables 43 and 44.

151

Table 43

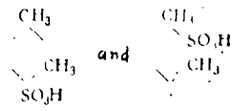
a)	b)	c)	d)
e)	144,0	−25,0	0,881
f)	139,3	−47,4	0,867
g)	138,5	−13,2	0,861
h)	136,2	−94,4	0,864

a) Compound; b) Boiling point, °C; c) Melting point, °C; d) Specific gravity $d_{4^\circ}^{20^\circ}$; e) Ortho-xylene; f) Meta-xylene; g) Para-xylene; h) Ethylbenzene

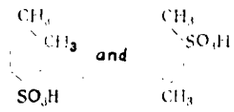
Table 44

Compound	Solubility in 100 gm of, at 15°		
	Water	Absolute Alcohol	Ether
Ortho-xylene	Insoluble	Soluble in any quantity	Soluble in any quantity
Meta-xylene	Insoluble	[illegible]	[illegible]
Para-xylene	Insoluble		
Ethylbenzene	0,01		

152 When strong sulfuric acid is reacted with xylenes, the reaction with the meta-isomer goes most readily, and results in formation of meta-xylene-4-sulfonic acid and meta-xylene-2-sulfonic acid:



Ortho- and para-xylenes react with greater difficulty with sulfuric acid because of the difference in the effect of the methyl groups upon the orientation of the sulfo group. The reaction products are [illegible] ortho-xylene-4-sulfonic acid and para-xylene-2-sulfonic acid (Bibl.116):



152 At 100°, weak nitric acid (30% HNO_3) oxidizes ortho- and para-xylene to the corresponding toluic acids; meta-xylene does not react under these conditions. A mixture of chromic and sulfuric acids oxidizes ortho-xylene to CO_2 and H_2O, and meta- and para-xylenes to phthalic acids (Bibl.117).

Xylene is obtained in the coking of coal and in the pyrolysis of petroleum products.

Table 45

Compound	Composition of Xylene, %	
	From Coal	From Petroleum
Meta-xylene	65—70	29—31
Para-xylene	12—15	8—11
Ortho-xylene	5—8	23—27
Ethylbenzene	8—10	21—23
Gasolines	1—2	13—15

Technical xylene consists of all three isomers and of ethyl benzene, and also contains small amounts of trimethylbenzene and gasolines. Composition of coal xylene differs sharply from the petroleum product (Table 45) (Bibl.117,118) in that it has a greater content of meta-isomer and a lower content of ethyl benzene and paraffins.

Due to the small difference in their boiling points, these hydrocarbons cannot be separated by distillation.

Separation by freezing (Bibl.119) or by employment of the differences in the solubilities of the calcium salts of their sulfonic acids (Bibl.120) also does not yield satisfactory results. The most valuable, for purposes of nitration, meta-xylene, may be separated by subjecting technical xylene to sulfonation by sulfuric acid (96% H_2SO_4) at 50 - 55°. This results in the sulfonation of, and the entry into solution merely of the ortho- and meta-isomers, while the para-xylene, the ethyl benzene, and the gasolines are separated out.

The ortho- and meta-xylene sulfonic acids are decomposed by steam, the meta-xylene-sulfonic acid decomposing between 130 - 140°, and the ortho-xylene sulfonic acid

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152 decomposing at 160°. The liberated hydrocarbons were driven off with the water vapor and separated from the water vapor in a condenser (Bibl.121).

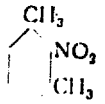
Purification of technical xylene to be nitrated is unprofitable, when performed in the manner described.

Therefore, it is primarily xylene derived from coal, which contains the largest amount of meta- and para-isomers, that is chiefly employed in nitration. The content of other impurities is limited by the technical specifications, in accordance with xylene has to have a specific gravity of 0.863 ± 0.003, must go over in the 137.5 - 141.5° temperature interval, and not less than 95% of xylene must go over in a temperature range of no more than 4.5°.

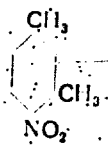
Mononitroxylene. When technical xylene is nitrated by mixed sulfuric and nitric acid, technical mononitroxylene is formed.

$$C_6H_4(CH_3)_2 + HNO_3 \rightarrow C_6H_3(CH_3)_2(NO_2) + H_2O.$$

153 The nitration product is a mixture of isomers. Thus, nitration of meta-xylene results in the formation of three isomers (Bibl.122, 123), chiefly

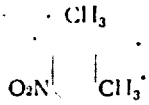


2-nitro-meta-xylene and



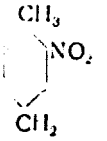
4-nitro-meta-xylene,

as well as a small amount of



5-nitro-meta-xylene.

Nitration of para-xylene results in the formation only of



2-nitro-para-xylene

It is more difficult to nitrate ortho-xylene than the meta- and para-isomers

[illegible]

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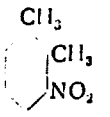
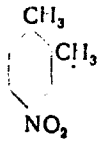
153 (Bibl.127), and two isomers (Bibl.128) are formed as a consequence:


3-nitro-ortho-xylene and


4-nitro-ortho-xylene

Kobe and Pritchett (Bibl.129) have investigated the effects of various factors upon nitration of ortho-xylene to the mononitroderivative. They determined that, when the optimum conditions are adhered to, a yield of 90% mononitroorthoxylene may be achieved. The nitration product consists of 58% 3-nitro- and 42% 4-nitro-ortho-xylene.

Of the three xylene isomers, meta-xylene is nitrated most readily (Bibl.123, 130). Nitration of meta-xylene requires half as much sulfuric acid as does nitration of the ortho- and para-isomers.

Table 46 presents a comparison of the conditions of nitration of the isomers of xylene.

Table 46

a)	b)		e)	f)		g)	h)
	c)	d)		d)	c)		
ortho-(2,3)-	6—35	25	15,8	80	78—82	60	90
para-(2,5)-	20—40	30	5,0	85	77—85	30	92
meta-(1,03)-	5—55	30	10,0	81	77—85	60	98

a) Molar ratio $\frac{\text{xylene}}{H_2SO_4}$; b) Temperature °C; c) Permissible; d) Optimal; e) Excess HNO_3, %; f) Strength of H_2SO_4, %; g) Reaction time, min; h) Maximum yield, %

Nitration of ethyl benzene forms a mixture of three isomers: ortho-, para-, and meta-. The technical product, obtained at 35 - 40°, consists of 48.5% para-, 45% ortho-, and 6.5% meta-nitro-ethylbenzene (Bibl.131, 132).

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154 Para-nitroethylbenzene was recently suggested as the starting material for the production of an important pharmaceutical, synthomycin, and a continuous method of producing mono-nitroethylbenzene, with subsequent separation of para-nitro derivatives, has been developed for this purpose.

The physical properties of the various nitroxylene and nitroethylbenzene isomers are presented in Table 47.

Table 47

Chemical	Specific Gravity at 15°	Boiling Point °C	Melting Point °C	Appearance under Normal Conditions
2-Nitro-meta-xylene				Light yellow liquid
4-Nitro-meta-xylene	1.112	225	13	The same
5-Nitro-meta-Xylene	1.135	237	2	Elongated needles
2-Nitro-para-xylene	1.142	273 239	74 —	Light yellow liquid
3-Nitro-ortho-xylene		240	15	The same
4-Nitro-ortho-xylene	—	228	11	Yellow prisms
Ortho-nitroethylbenzene		243 246	—11,5 37	Yellow liquid
Para-nitroethylbenzene				The same
Meta-nitroethylbenzene				The same

Dinitroxylene. When technical mononitroxylene is nitrated with mixed acid, technical dinitroxylene results:

$$C_6H_3(CH_3)_2(NO_2) + HNO_3 \rightarrow C_6H_2(CH_3)_2(NO_2)_2 + H_2O.$$

The nitration product is a mixture of isomers. Thus, 2-nitro-meta-xylene has two isomers: primarily 2,4-dinitro-meta-xylene, and a small amount of 2,5-dinitro-meta-xylene. The 4-nitro-meta-xylene isomer yields primarily 2,4-dinitro-meta-xylene; 4,6-dinitro-meta-xylene, and a small amount of 4,5-dinitro-meta-xylene. The 5-nitro-meta-xylene isomer yields 4,5-dinitro-meta-xylene.

The 2-nitro-para-xylene isomer yields primarily: 2,6-dinitro-para-xylene,

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154 2,3-dinitro-para-xylene, as well as a small amount of 2,5-dinitro-para-xylene. The 3-nitro-ortho-xylene isomer yields (Bibl.128) 3,4-dinitro-ortho-xylene, 3,6-dinitro-ortho-xylene and 3,5- or 4,6-dinitro-ortho-xylene. The 4-nitro-ortho-xylene isomer yields 4,6-dinitro-ortho-xylene, 3,4-dinitro-ortho-xylene, and 4,5-dinitro-ortho-xylene (Bibl.132).

For all practical purposes, the ortho- and para-nitroethylbenzenes yield only 2,4-dinitro-ethylbenzene. The meta-dinitroethylbenzene usually oxidizes as early as the conditions obtaining in the second phase (Bibl.133).

The physical properties of the various isomers of the dinitroxylenes and dinitroethylbenzene are illustrated in Table 48.

Trinitroxylene. When technical dinitroxylene is nitrated with mixed acid, technical trinitroxylene is formed:

$$C_6H_2(CH_3)_2(NO_2)_2 + HNO_3 \rightarrow C_6H(CH_3)_2(NO_2)_3 + H_2O.$$

As was shown by I.I.Sidney, the speed of this reaction under homogeneous conditions is quite high, and does not diminish under heterogeneous conditions. This last is explained by the fact that the trinitroxylene obtained under conditions of nitration
155 is liberated in the form of solid product and therefore does not dissolve dinitroxylene (unlike TNT, which is in the liquid state under these conditions), and consequently, does not reduce the strength thereof.

The nitration product of technical dinitroxylene is a mixture of isomers. Thus, 2,4-dinitro-meta-xylene yields two isomers: primarily 2,4,6-trinitro-meta-xylene, and a very small quantity of 2,4,5-trinitro-meta-xylene. The 2,5-dinitro-meta-xylene isomer yields 2,4,5-trinitro-meta-xylene. The 4,6-dinitro-meta-xylene isomer yields primarily 2,4,6-trinitro-meta-xylene and a very small amount of

155

Table 48

Compound	Melting Point oC	Appearance	Solubility, gm, in 100 cc 95% Alcohol	
			at 15°	at 20°
2,4-Dinitro-meta-xylene	83	White platelets	-	-
2,5-Dinitro-meta-xylene	102	Colorless needles	-	-
4,6-Dinitro-meta-xylene	93	-	-	-
4,5-Dinitro-meta-xylene	132	-	-	-
2,6-Dinitro-para-xylene	124	Thin needles	-	-
2,3-Dinitro-para-xylene	93	Monoclinic prisms	-	-
2,5-Dinitro-para-xylene	148	Yellow needles	-	-
3,4-Dinitro-ortho-xylene	82	Silky needles	-	-
3,5-Dinitro-ortho-xylene	90	-	-	-
4,5-Dinitro-ortho-xylene or 3,5-dinitro-ortho-xylene	96-98	Transparent needles	-	-
3,4-Dinitro-ortho-xylene	115	White needles	-	-
2,4-Dinitroethylbenzene	4	Oily liquid	-	-
2,4,6-Trinitro-meta-xylene	182	White crystals of rhombic form, spec. grav. 1.75	0.324	0.339
2,4,5-Trinitro-meta-xylene	96	Triclinic crystal	-	1.88
4,5,6-Trinitro-meta-xylene	129	Monoclinic crystal	-	0.205
2,3,6-Trinitro-para-xylene	144	Yellow needles	0.32	-
3,4,6-Trinitro-ortho-xylene	115	Colorless needles	1.139	-
3,4,5-Trinitro-ortho-xylene	72	Yellow needles	0.274	-
2,4,6-Trinitro-ethyl-benzene	97	Colorless needles	-	-

4,5,6-trinitro-meta-xylene. The 4,5-dinitro-meta-xylene isomer yields 4,5,6-trinitro-meta-xylene.

When pure meta-xylene is nitrated to the trinitro compound, it is primarily the 2,4,6-trinitro-meta-xylene isomer that is obtained, which contains only traces of the other isomers (Bibl.134).

The theoretical yield of product is 88% of the theoretical. Nitration goes easily, and requires a 60% excess of nitric acid.

156 All three isomers of ~~XXIXIX~~ dinitro-para-xylene, 2,6, 2,3- and 2,5- yield 2,3,6- or 2,3,5-trinitro-para-xylene, at 62 - 63% of the theoretical (Bibl.123, 135).

Nitration of para-xylene goes with greater difficulty than that of meta-xylene.

154 Upon nitration of the XX 3,4- and 3,6-dinitro-ortho-xylenes, 3,4,6-trinitro-ortho-xylene is formed, while nitration of 4,5-dinitro-ortho-xylene results in the formation of 3,4,5-trinitro-ortho-xylene. Nitration of 3,5- or 4,[illegible]-dinitro-ortho-xylene yields XX 3,4,5- or 3,4,[illegible]-trinitro-ortho-xylene (Bibl.128, 135).

Ortho-xylene nitrates with considerably more XXXXXXXX difficulty than meta- and para-xylene. Its nitration to the trinitro compound results in the production of an oil which freezes with difficulty at 15 - 18°. The yield of trinitro-product is about 54-55% of the theoretical (Bibl.135).

When ethyl benzene is nitrated to the trinitro derivative, usually, a single isomer, 2,4,[illegible]-trinitroethylbenzene is formed. The nitration of ethyl benzene under the same conditions as xylene XXXXXX leads to incomplete conversion to the trinitro compound. The product contains a considerable quantity of dinitro derivative and is an oily substance that does not solidify XXXXXXXX even at XXXX -20°C (Bibl.136).

Table 49

Solvent	Solubility, gm, of 2,4,[illegible]-trinitro-meta-xylene (in 100 gm of solvent)	
	at 20°	at Boiling Point
Benzene	[illegible]	7.5
Toluene	[illegible]	[illegible]
Ethyl alcohol	[illegible]	[illegible]

The yield of this product, calculated as trinitro compound, is [illegible]%. It should be noted that, due to the length of the side chain, a considerable part of the ethyl benzene and its nitro derivatives XX oxidize, under conditions of nitration, to nitrobenzoic acids (Bibl.137).

The physical properties of the various trinitroxylene isomers (Bibl.138, 139) are illustrated in Tables 48 and 49.

The quality of technical xylene is dependent, primarily, upon the composition of the xylene being nitrated. Only the meta- and para-xylenes yield a quality non-oily

156 product (Ibid.140). The trinitro derivatives of the meta- and para-xylenes form a eutectic mixture of the following composition: 76% trinitro derivatives of para- and 24% trinitro derivative of meta- melting at 12[illegible] - 127°.

Inasmuch as the technical product always contain more meta- than para-isomer, these two isomers usually yield trinitroxylene with a melting point of 170 - 176°, corresponding to a content of 80 to 90% of trinitro-meta-xylene, and from 20 to 10% trinitro-para-xylene.

Mixtures of the nitro derivative of orthoxylene and ethyl benzene yield a liquid oily product from which the solid trinitroxylene has to be cleansed.

As the meta-xylene nitrates more readily than do other isomers, an attempt was made to create conditions of nitration such as to nitrate the meta-xylene to mononitroxylene, without nitrating the other isomers, and only then to drive off the incompletely nitrated components from the mononitroxylene. However, work has shown that it is not possible to nitrate meta-xylene to mononitroxylene without nitrating the other isomers.

In industry, technical xylene is nitrated to trinitroxylene, and only then are the liquid oily products separated from the main product. The separated liquid oily products are called xylene oil. The separation of the bulk of the oil from the product is performed by treating with hot water on a centrifuge, and the residual oil is removed by use of a solvent (extraction).

157 The technical xylyl, freed of the oil, is a fine crystalline substance, white or slightly yellowish in color. The freezing point of the purified product is 170 - 176°, its specific gravity 1.65, its gravimetric density 0.6. Xylyl is virtually insoluble in water, dissolves poorly in alcohol, and/in a mixture of alcohol and benzene

157 (Table 50). Xylyl dissolves rather well in benzene and acetone.

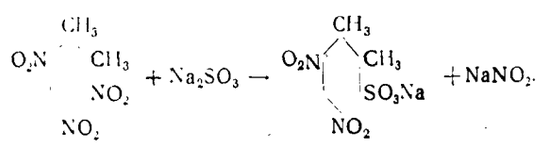
Xylyl is a neutral substance that does not react with metal. Like TNT, xylyl yields metallic derivatives with alcoholic bases, and these metallic derivatives have a detonation point in the range of 142 - 165°, and a shock sensitivity less than that of mercury fulminate, but higher than that of lead azide. For this reason, washing with caustics is ruled out in the production of xylyl.

Table 50

Volumetric Ratio of Solvents in Mixture		Solubility of Xylyl, %, at Various Temperatures °C	
Alcohol	Benzene	20	80
0,5	1	0,71	--
1,0	1	0,45	0,32
1,5	1	0,29	0,24
2,0	1	0,2	--

Xylyl does not form salts in ammonium-alcohol solution, and does not react with gaseous ammonia (Bibl. 4, 141), whereas, under these circumstances, TNT forms compounds that are dangerous to handle. This property makes it possible to recommend xylyl strongly for the production of ammonites. However, it must be borne in mind that the presence of moisture, as well as conditions of low temperature, facilitate onset of reaction between xylyl and ammonia. Caustic and carbonate bases act upon xylyl to form metallic xylyl derivatives of greater sensitivity than xylyl.

An aqueous solution of sodium sulfite does not act upon trinitro-meta-xylene, but does react with other trinitro derivatives of xylene, to form soluble sulfur salts. The reaction follows the following equation



However, the purification of xylyl by an aqueous sodium sulfite solution does not, despite the substantial losses of xylyl, yield a completely oil-free product, inasmuch

157 as the sodium sulfite does not react upon the nitro derivatives of ethyl benzene.

The treatment of technical ~~xylyl~~ xylyl with a 5% sodium sulfite solution at 60°, for three hours, result increasing the freezing point from 1.2 - 1.3° to 1.8°. The treatment with a 7 - 9% sulfite solution at 70° for four hours yields a product having a freezing point of 17.4°, but losses attain 24% in this process.

With respect to heating, xylyl is very highly stable and, despite the high melting point (170 - 180°), it fuses without decomposition. Its detonation point is about 330°.

When compared with TNT, xylyl is somewhat more sensitive to shock and less receptive to detonation.(the minimum initiating charge of mercury fulminate for compressed xylyl is about 0.2 gm, whereas for TNT it is 0.38 gm). Xylyl, freed of oily impurities, causes 270 cc expansion in the Trauzl block, while its brisance
158 is 16 mm on the Hess scale, while detonation velocity is 7000 m/sec. Thus, xylyl is inferior to TNT in explosive properties.

Xylyl is employed to fill munitions in alloys with TNT, in mixtures with ammonium nitrate, and is also capable of being used in the pure form. A composition of 50% NH_4NO_3, 37.5% TNT, and 12.5% xylyl is used to fill shells, whereas one consisting of 82% NH_4NO_3 and 18% xylyl is used to fill mines and hand grenades. The mixture of 88% NH_4NO_3 and 12% xylyl is used for underground work.

Xylyl oil, which is a by-product of xylyl production, is used as a plasticizer in the manufacture of powder, and as a component of dynamite.

Section 2. Trinitroxylene Production Technology.

Xylene undergoes nitration more readily than toluene, thanks to the fact ~~XX~~ that it contains two metal groups, but it also oxidizes and undergoes resinification more

~~XXXXXXX~~

158 readily. The intensity of the oxidizing processes also increases as a consequence of the presence of ethyl benzene in technical xylene (the ethyl benzene is oxidized more readily than the xylene). Xylene may be nitrated to trinitroxylene in one, two, and three stages.

The method of nitration of xylene in a single stage, developed by A.A.Solonina, was put into effect during World War I at three plants in Russia. Under this method, xylene was nitrated by gradually running it into the mixed acid (70% H_2SO_4, 18% HNO_3, and 3% H_2O) at 35°. The excess nitric acid was 45% of the theoretical. Upon

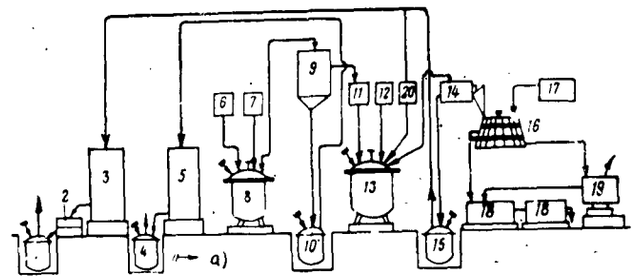


Fig.56 - Diagram of Xylyl Production

1,4,10, and 15 - Rising devices; 2,14 - Vacuum funnels; 3 and 5 - Settling columns; 6,7,11,12,17, and 20 - Measuring vats; 8 and 13 - Nitrators; 9 - Separator; 16 - Washing vat; 18 - Traps; 19 - Centrifuge

a) Compressed air

completion of run-in, it was held at 105° for an hour. The xylyl was then separated from the spent acid on a vacuum funnel, and sent to the washing vat, where it was washed free of acid. The washed xylyl was centrifuged and sent to drying. The resultant product had a freezing point of 163 - 165° (Bibl.138).

A shortcoming of the single-stage method is the large yield of acids and the low quality of the xylene. A certain advantage is the minimum need for equipment and the

158 simplicity of the technological process.

Another economical method is the two-stage procedure, in accordance with which, the xylene was first nitrated to mononitroxylene, whereupon the mononitroxylene was nitrated to trinitroxylene. The two-stage method was introduced into industrial practice in a somewhat modified variant.

Specifically, the first stage consists of nitration of xylene to dinitroxylene, whereas in the second, trinitroxylene is produced. Under this nitration procedure, all the spent acid is employed for the first stage, acid circulation is closed, and this reduces the acid consumed in nitration.

The three-stage method yields even greater economy of acid than does the two-stage, but the technological process is further complicated under this method (Fig.140).

The production of xylyl in the two-stage method is illustrated in Fig.[illegible].

159 The mixed acid is poured from the measuring tank (1) into the nitrator (8), and xylene is then gradually added from the measuring tank (7). When nitration is completed, the nitro mass is forced into a separator (9), by compressed air, and separation of the fused dinitroxylene from the spent acid is performed there. After separation, the fused dinitroxylene is emitted into the measuring tank (11), and the spent acid into the rising device (10), from which it is transmitted, by compressed air, to the settling column (5). After settling, the spent acid is delivered by rising device (4) to denitration.

The second stage of nitration is run as follows. Spent acid is run into nitrator (13) from measuring tank (20), and mixed acid is run in from measuring tank (12), whereupon nitration is performed by slowly running molten dinitroxylene into the apparatus. Upon completion of the process, the nitro mass is transferred to the vacuum funnel (14), with the agitator operating. Compressed air is used to effect the

159 transfer. The spent acid is collected in rising device (15), which, as required, functions either as a vacuum collector or as a rising device.

From rising device (15), the spent acid is forced partially to measuring tank (20), the rest going to the settling column (3). After settling, the acid is filtered through funnel (2), and sent on to rising device (1), which, like receiver (15), functions either as a vacuum receiver, or as a rising device, depending upon necessity. The secondary spent acid is transmitted by compressed air from rising device (1), to the acid mixing shop to make up the first-stage mixed acid.

The xylyl, separated from the acids, is transferred to the washing vat (11). Washing is performed first with cold, and then with hot water, from measuring tank (17). After each washing, the wash water is allowed to stand, and then it is poured into a system of traps (18), from which it goes to the sewerage system. Upon completion of the washing, the xylyl, along with the final wash water is drained, with agitator functioning, into centrifuge (11), where the water is separated out, and the product is then again treated for a brief period with hot water and steam to eliminate the bulk of xylyl oil. The xylyl oil goes to a trap along with the wash water, and accumulates on the bottom of the trap. The xylyl, washed free of acids, and centrifuged free of water, is emptied from the centrifuge into wooden boxes and is then taken, on a car, for final purification from oil.

The apparatus employed is standard. The cast iron nitrators have jackets, coils, and a propeller stirrer making 160 rpm. A separator is mounted on the agitator shaft at the level of the surface of the liquid. The separating funnel is vertical, has a conical bottom, and a side tap for removal of the nitro product. It is made of iron or cast iron. The metering tank for the dinitroxylene is iron, and provided with

159 a coil.

The vacuum-funnel casing is iron, and the filtering surface is a porous ceramic plate. Side hatches are provided in the vacuum-funnel to discharge the product. The decanters for water washing of the product are wooden, conical vats, having a wooden frame stirrer, and two drainage apertures: one for water (at the side wall) and one for products (at the bottom). The capacity of the vat is 5 m^3.

In the first stage of nitration, a mixed acid of nitric acid and secondary spent acid is employed. Its composition is: 41 - 42% H_2SO_4; 18% HNO_3; 3% N_2O_3; 4% nitro product and 32 - 33% H_2O. The amount of mixture for nitration is taken to provide a 10% excess of nitric acid.

The xylene is added to the mixed acid with a gradual rise in temperature to 50° over a two-hour period, whereupon the nitro mass is held for half an hour at 80°. Upon completion of the process, the nitro product should have a specific gravity of 1.3, and its freezing point should be in the range between 18 and 33°. The yield is 96 - 98% of the theoretical.

The acid mixture for the second stage has the following composition: 82% H_2SO_4 and 14% HNO_3. The quantity of mixture employed is calculated to yield a 50% excess of HNO_3. In order to increase the module, spent acid is added in the amount of 1 part by weight to 1 part by weight of dinitroxylene. The run-in of dinitroxylene into the mixed acid is performed with gradual elevation of the temperature from
160 70 to 80°, over a two-hour period. Then the nitro mass is held at 120° for an hour, whereupon it is cooled to 25 - 30° at the conclusion of the process. If the mass is sent to the vacuum filter in the uncooled state, dissolved oil, which will rapidly clog the pores of the filter, will separate out of the spent acid as it cools in the

160 pores of the ceramic plate.

The quality of xylyl is largely dependent on the manner in which the process of nitration is performed. If the conditions of nitration are violated, the resultant xylyl is in the form of very fine crystals. This complicates further processing, particularly filtering, as the pores of the filter rapidly clog. Nitration by strong acid mixtures at 50 - 75°, and holding at 120°, facilitate the formation of larger crystals. It should be noted that an increase in temperature before holding must be done very carefully, inasmuch as a rise in temperature is accompanied by a sharp increase in the oxidation of the nitro derivatives of the ortho- and para-xylenes, as well as ethyl benzene. This is accompanied by abundant separation of nitrogen oxides. The separation of the gas results in foaming of the nitrator contents. This may result in overfilling of the apparatus with foam. This is combated by energetic stirring and cooling. As a consequence of oxidation of the impurities, the quality of the xylyl is somewhat impaired.

As a result of nitration, xylyl is obtained with a freezing point of about 155 - 162°. This is unsuited to military needs and requires purification. Xylyl of this kind is a semi-solid, containing about 28 - 30% of liquid nitro derivative (nitro derivative of ortho-xylene, ethyl benzene, and the products of the lower stages of nitration of para- and meta-xylenes). The oily impurities in the xylene reduce its susceptibility to detonation. Moreover, as has been pointed out by A.G.Gorst (Pibl.138), during World War I, an oily liquid was observed to leak out of shells filled with an alloy of TNT and xylyl. This impaired the physical structure of the shell.

In France, purification of the xylyl of oil was performed by washing it in five times its quantity of cold alcohol. As a consequence of the lower solubility of

meta-xylene trinitro derivatives in alcohol, the meta-xylene was obtained in virtually pure form, with a yield of about 75%. Because of the large amount of alcohol expended (with considerable losses upon washing and recovery), this method is unprofitable.

The spent acid from stage one, and a mixture of gasoline and benzene were tried as solvents for the oil, in the washing of xylyl. Utilization of this type of acid renders denitration more difficult, and results in losses of liquid nitro derivatives. Utilization of a mixture of gasoline and benzene is not very profitable. The cost of purification rises as a consequence of the loss of solvents upon washing and recovery. Use of these solvents is inconvenient due to toxicity and the danger of fire.

The most practical method of removing oil from xylyl is that of washing it with hot water on the centrifuge, where a considerable quantity of oily impurities is removed. The xylyl going to washing contains 28 - 32% oil, and 15 - 18% after washing, and has a freezing point of 1.5 - 1.8°. The removal of oil from xylyl washed on the centrifuge is illustrated in the diagram in fig.5".

Xylene is measured into extractor (1) from metering tank (2), and the xylyl is charged in by hand, batch-wise, through the hatch, with the stirrer in operation. Upon the completion of extraction (1 - 1.5 hrs), the mixture is allowed to stand, and the xylene, saturated with xylyl oil, is forced into collector (4) of oily xylene, by compressed nitrogen. After removal of the bulk of the xylene, water is run into the extractor from the metering tank (3), and, with agitator operating, the entire mass is emptied into the centrifuge (5), where the xylyl is separated from the water, and the xylene residues. The xylyl is washed on the centrifuge with warm water to full removal of the mother xylene (the wash water should then be transparent).

The water from the centrifuge, containing xylene, flows into receiver (6), from

which it goes to Florentine receiver (7), in which the water is separated from the xylene. The water passes through a trap into the sewerage system, and the xylene to receiver (8), from which it is transferred to the main collector (4).

Xylene can be completely separated from xylyl on a centrifuge, but when this is done, losses due to evaporation are great.

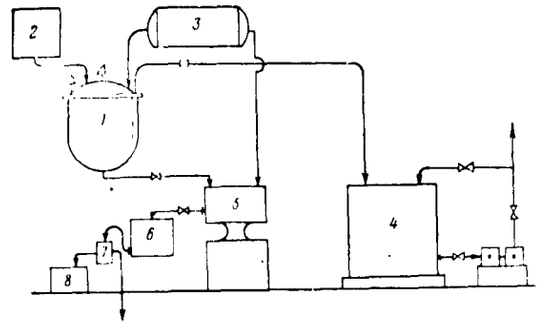


Fig.5 - Diagram of Purification of Xylyl

1 - Extractor; 2 and 3 - Metering tanks; 4 - Collector; 5 - Centrifuge; 6 and 8 - Receivers; 7 - Florentine receiver

The xylyl freed of oil, and now containing only 2.5 - 3.5% oil, is removed for drying in wooden boxes on cars. This product has a freezing point of 173 - 175°.

In extraction, 0.5 - 0.75 parts of xylene per weight are employed per part xylyl by weight. As a consequence, the mother xylene obtained contains 17 - 25% oily impurities, and a specific gravity of 0.96 - 0.98. The mother xylene is sent to nitration. Thus, employment of the xylene as a solvent for purification of xylyl has the advantage that the mother liquor does not require regeneration.

No more than 16 - 18% of oil accumulates in the xylyl going to extraction, because all the surplus oil is drained out along with the water, when the xylyl

161 is washed on centrifuges.

The xylyl is dried for 12 hrs in a tunnel dessicator by air heated to 70 - 72°. Before drying, the xylyl is rubbed through a No.10 sieve.

The yield of pure xylyl is 48 - 49% of the theoretical.

Xylene from petroleum may also be employed to produce trinitroxylene. The technological process is the same, with the single difference that the amount of nitric acid used for nitration, as well as the amount of nitro mixture is computed not on the basis of the entire initial product, but only on the basis of the aromatic portion thereof. The amount of excess nitric acid provided in each phase is the same as before.

In the nitration of petroleum xylene, certain fire danger exists because of the presence of gasoline, particularly in the second stage, where a higher temperature is maintained. However, thanks to the fact that the bulk of the gasolines ~~are~~ removed with the fumes in the first stage, the fire danger in the second stage is not as great.

Xylyl obtained from petroleum xylene contains considerably more oil than that from coal xylene. In order, in part, to get rid of the oil, the spent acid from the

162 second process is diluted with spent acid from the first process, until an 83% sulfuric acid content is attained. As this occurs, 0.11 part of oil separates out per part of initial xylene by weight. The dilute spent acid is permitted to settle free of the oil, whereupon the acid is removed by separation, and is then sent in its entirety to make up the first-stage nitro mixture.

When petroleum xylene was nitrated, the dinitroxylene was separated from the gasolines by solution of the dinitroxylene in 98% sulfuric acid, followed by separation. Further, the dinitroxylene, dissolved in sulfuric acid, was nitrated. The second-stage

spent acid was diluted with first-stage spent acid for partial separation of the dissolved xylyl oil, before being sent to be used in making mixed acid (for the first stage).

E. Dinitronaphthalene and Other Nitro Derivatives of Naphthalene

The nitro derivatives of naphthalene, and particularly dinitronaphthalene (a mixture of the 1,5 and 1,8 isomers) employed in filling shells, are considerably less powerful than the nitro derivatives of toluene. Nevertheless, there is adequate reason for producing dinitronaphthalene as an explosive, as this makes possible the use of an additional source of raw material - naphthalene.

In view of its low explosive properties (detonation velocity 1150 m/sec, expansion in Trauzl block 100 cc, compression of lead cylinder 4 mm) and its low detonation sensitivity, dinitronaphthalene is not employed as an independent explosive. It is widely employed as a combustible component in explosives used in military engineering and in mining.

Thus, dinaphthalite, containing 12% dinitronaphthalene and 88% ammonium nitrate, is employed to fill certain types of artillery shells and mines. A mixture consisting of 20% dinitronaphthalene and 80% TNT is employed to fill aviation bombs. Granular dinaphthalite No.1, consisting of 12% dinitronaphthalene and 88% ammonium nitrate, is widely employed as a moisture-resistant high explosive in underground explosions, and no danger from gas or dust is involved. Dinaphthalite reveals a 360 cc expansion of the Trauzl block and a brisance of 14 - 17 mm, which permits the conclusion that it is a good ammonium nitrate explosive for resistant rocks.

162 Section 1. Chemistry of Production; Properties and Applications of Nitro Derivatives of Naphthalene

Nitronaphthalenes are produced in the nitration of naphthalene, usually as a mixture of various isomers, the number of which increases with increase in the degree of nitration. In practice, the possible maximum degree of nitration of naphthalene by mixed sulfuric and nitric acid corresponds to the production of tetranitronaphthalene. Penta- and hexa-nitronaphthalenes are produced indirectly.

The initial product is naphthalene, which is contained in relatively large quantity in coal tar (10 - 11%)*. This is particularly the case in medium and heavy oils, as well as in certain grades of petroleum, from which it is extracted by fractional distillation. The separated naphthalene is subjected to purification by caustic and sulfuric acid, with subsequent vapor distillation or volatilization.

Naphthalene is readily volatilized and sublimated. It is volatile with steam. Naphthalene crystallizes as gleaming white platelets melting at 80° and boiling at 218°. Its specific gravity at 25° is 1.151, and at 80° - 0.9790. The latent heat of fusion is 34.39 kcal/kg.

163 Naphthalene is weakly soluble in water (0.003 gm dissolves in 100 gm of water at 25°), and is readily soluble in hot alcohol, ether, benzene, and acetone. It is readily distillable in a stream of steam.

The solubility of naphthalene at 16.5° in 100 gm toluene is 31.94 gm, and at 15° in 100 gm absolute alcohol it is 5.29 gm.

When naphthalene is oxidized with weak nitric acid, potassium bichromate, or potassium

[illegible]

*The yield of coal tar in the coking of Donets coals is 2 - 3% of the amount of coal charged. This tar contains up to 12.4% napthalene (Bibl.142).

permanganate, phthalic acid is formed: $C_6H_4(COOH)_2$. With picric acid it forms the following molecular compound:

$$C_{10}H_8 + C_6H_2(NO_2)_3OH \rightarrow C_{10}H_8 \cdot C_6H_2(NO_2)_3OH$$

in the form of golden yellow crystals having a melting point of 149° and soluble in alcohol, ether, and benzene. Upon boiling with water, this compound decomposes. This reaction is employed for quantitative determination of naphthalene.

Naphthalene yields similar compounds with many other derivatives of the aromatic hydrocarbons, and, with each of the isomers of the di- and trinitro-derivatives, it forms a characteristic compound, different from the others. When reacted with lead tetraacetate in acetic acid solution, the naphthalene is transformed into an acetyl derivative (Bibl.143).

When hydrogen atoms are replaced by identical radicals, naphthalene is capable of yielding: two monosubstituted products (α or β), ten di-substituted, fourteen tri-substituted, and, further, twenty-two tetra-, fourteen penta- , ten hexa-, two hepta-, and one octa-isomeric derivative.

Thanks to the specific structure of naphthalene, it has a number of distinctive features, the most significant of which are the following (Bibl.144):

a) the reactivity of naphthalene is greater than that of benzene. It oxidizes, reduces, and undergoes substitution more readily, particularly in the α-position;

b) the formation of molecular compounds goes more easily with naphthalene than with benzene. This may relate to the fact that naphthalene is less saturated than benzene;

c) hydrogenation of naphthalene goes more easily than that of benzene;

d) the properties of the mono-derivatives of naphthalene differ noticeably from

163 the mono-derivatives of benzene. Moreover, the substituting group reveals a specific influence upon the ring in which it is found, and upon the adjacent one;

e) the substitution reaction in the naphthalene ring, even in the production of mono substitutes, is very complex: thus, the α-position is considerably more reactive than the β-position. However, at high temperatures, when thermodynamic equilibrium is achieved more rapidly, one will get, to cite an example, the β naphthalene sulfonic acid, and not the α.

Data on the heat of combustion and the formation of naphthalene and its nitro derivatives are presented in a work by Rodosche (Bibl.145), and in Appendix 18.

The following specifications must be met by naphthalene: temperature of crystallization 79.8°, and 0.003 - 0.005% ash content. The degree of purification is also determined by the coloration induced by sulfuric acid.

For military purposes, naphthalene is employed not only to produce nitro derivatives therefrom, but directly as a combustible or a smoke-forming component in various mixtures.

Naphthalene is widely employed in the production of phtalic anhydride, dye synthesis, the making of plastics, etc.

Liquid products of naphthalene hydrogenation - tetralin and dekalin yield nitro derivatives, and may consequently be used as raw materials for the production thereof. They are also technical solvents and are, in addition to this, employed as fuels for engines.

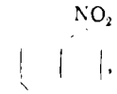
The production of naphthalene has reached large figures in all countries. In the USA (Bibl.14f), the discovery of a method of catalytic oxidation of raw naphthalene by air in phthalic anhydride has considerably increased the demand for

naphthalene. Phthalic anhydride has come into large-scale use for the production of synthetic resins, dibutyl phthalate, anthraquinone, benzoic acid, etc. Its production attained 20,000 tons in 1940. In England (Bibl.347), a production of naphthalene from coal reached 80,000 tons in 1943. In Germany, more than 40,000 tons of naphthalene was produced per year in the prewar years.

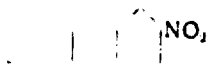
Mononitronaphthaline is formed upon nitration of naphthalene with nitric acid or mixed sulfuric and nitric acids:

$$C_{10}H_8 + HNO_3 \rightarrow C_{10}H_7NO_2 + H_2O.$$

The nitration product is an α-isomer



containing traces of β-isomer



and the oxidation products: nitrobenzoic $C_6H_4(NO_2)COOH$ and nitrophthalic $C_6H_3(NO_2)(COOH)_2$ acids, as well as nitronaphthols $C_{10}H_5(NO_2)_2OH$.

Under certain conditions of nitration (elevated temperature and strong mixed acid), the yield of side products increases. Thus, in technical mononitronaphthalene, [illegible] of β-nitronaphthalene and up to 3.0% 2,4-dinitro-1-naphthol was found (Bibl.148).

Technical mononitronaphthalene has a freezing point of 51 - 54°. The freezing point of β-mononitronaphthalene is 61°, and that of α- mononitronaphthalene is 79°.

α-Mononitronaphthalene crystallizes in the form of green and yellow crystals. [illegible] water, but is soluble in alcohol, ether, benzene, chloroform, and acetic acid. As distinct from the di- and trinitronaphthalenes, mononitronaphthalene dissolves readily in carbon disulfide.

The solubility of mononitronaphthalene in sulfuric and nitric acids is presented in Table [illegible].

Mononitronaphthalene is readily oxidized by an acetic acid solution bichromate in nitrophthalic acid. Weak alkaline solutions do not act upon mononitronaphthalene in the cold, and oxidation with formation of the oxy derivatives of naphthalene occurs only upon heating with strong solutions.

When sodium bisulfate is reacted with α-mononitronaphthalene, the result is 1-amino-naphthalene-4-sulfonic acid.

Studies [illegible] P.P.Shorygin and A.V.Topchyev (Bibl.149) have shown that

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Table 51

a)			b)		
c)	d)	e)	f)	d)	e)
50	41,0	0,38	50	39	0,14
50	64,5	0,75	50	58,5	0,22
50	84,0	1,12	50	70,5	0,29
60	21,5	0,36	60	37,5	0,13
60	35,0	0,72	60	55,5	0,20
70	14,0	0,28	60	66,5	0,27
70	23,0	0,42	70	21,0	0,06
70	32,0	0,56	70	32,0	0,12
80	24,0	0,81	70	46,0	0,19
—	—	—	70	53,5	0,25
—	—	—	70	58,5	0,31

a) Solubility in nitric acid; b) Solubility in sulfuric acid; ~~a)~~ ~~b)~~

c) Nitric acid strength, %; d) Temperature, °C; e) Solubility; f) Sulfuric acid strength, %

When naphthalene is nitrated at low temperatures to [illegible] (in the theoretical), α-mononitronaphthalene is formed yielding 90 - 98% of the theoretical. When the excess H_2SO_4 is great (as high as fourfold), and temperature is raised to 70°, 1,5-dinitronaphthalene is formed, along with the α-mononitronaphthalene. It should be noted that nitration under these conditions makes use only of 50% of the oxides, so that this method is of little value, practically speaking. These authors found that nitration of naphthalene by nitrous gases resulted in high yields of mononitronaphthalene, even at low temperature. On the basis thereof, they proposed that naphthalene be employed to absorb the "tailings" of gases of nitration installations, with the purpose of using them.

Earlier studies on the nitration of naphthalene by nitrous anhydride and the nitrosyl sulfuric acid (Bibl.150, 151, 152) were of no practical significance.

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1/5 A.V.Stepanov (Bibl.153), studied the nitration of naphthalene by sodium nitrate and other nitrate salts, noted the considerable reduction in the intensity of oxidizing processes, and the improvement in the quality of the products. However, the difficulties in the recovery of the spent acids, resulting from contamination thereof by sulfate salts, renders the employment of this method for practical roles to be out of the question.

Nitration of naphthalene has been performed with ~~XXXX~~ weak nitric acid, accompanied by the transmission of electric current (Bibl.154). This resulted in an increase in the yield of mononitro product (45.4% instead of 23.5%).

A number of further studies on the nitration of naphthalene (Bibl.155, 156) are known. At present, they are of purely historical interest in scientific terms. We note merely the research due to Oddo (Bibl.157), to arrive at a more precise knowledge of the mechanism of nitration of ~~XXXX~~ naphthalene and mononitronaphthalene. He performed nitration by first treating the naphthalene with nitric acid of 1.40 specific gravity, whereupon strong sulfuric acid was added thereto at 40°. The author came to the conclusion that the oily products he obtained by nitration are complexes of nitric acid and naphthalene.

Works due to A.I.Titov (Bibl.158) demonstrated the erroneousness of ~~XX~~ Oddo's contention. The complex he produced proved to be a solution of nitric acid and ~~XX~~ mononitronaphthalene. The conclusion that ~~XXX~~ 1,5-dinitronaphthalene allegedly ~~XXXXXXXXXX~~ predominated was also found to be untrue.

Matar (Bibl.159) studied the effect of the make-up of the mixed acid, the method of introducing the reactants, and the duration of the process, upon the degree of nitration of naphthalene.

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T.G.Aleksandrov and A.V.Shtam (Bibl.160) demonstrated that naphthalene would not react immediately with a mixed acid not containing nitrogen oxides. A certain time of induction is required, at the conclusion of which vigorous reaction sets in.

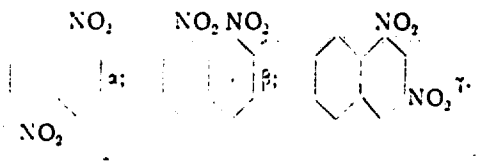
A.I.Titov, who observed the same phenomenon in the nitration of naphthalene by weak nitric acid (Bibl.158), holds that weak nitric acid nitrates only through the medium of nitrogen oxides, and a period of induction is required to form these. In the presence of nitrogen oxides, the reaction begins at once.

The nitration of naphthalene by nitric acid containing mercury nitrate, leads to the formation of nitronaphthols (Bibl.161).

Mononitronaphthalene is of very limited usefulness by itself.

In 1943, it was employed in Germany in smokeless low-heat powders (as 4% of the whole, replacing derivatives of the carbamide and urethane series, which were in short supply).

Dinitronaphthalene. Technical dinitronaphthalene is usually obtained by nitration of mononitronaphthalene by mixtures of sulfuric and nitric acids, or by nitric acid. The nitration product consists chiefly of the 1,5- or α-isomer, and the 1,8- or β-isomer, with a small admixture of the 1,3- or γ-isomer



The α- and β-isomers represent 40 and 40%, respectively.

The technical product also usually contains trinitronaphthalene, mononitronaphthalene, and nitronaphthols. For example, upon nitration of mononitronaphthalene with a mixture of sulfuric and nitric acids, a product of the following percentage compositions

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results (Bibl.142):

1,8-dinitronaphthalene	55.6
1,5- and 1,3-dinitronaphthalenes	32.6
α-nitronaphthalene	4.3
1, 4, 5- and 1, 3, 8-trinitronaphthalenes	4.23
Nitronaphthols (chiefly 2,4-)	1.2

Table 52 presents certain constants of the isomer dinitronaphthalene.

Table 52

Characteristics	1,5-Dinitronaphthalene	1,8-Dinitronaphthalene	1,3-Dinitronaphthalene
Melting point, °C	217	173.5	144
Shape of crystals	Yellow needles of a monoclinic system	Yellow rhombic platelets	Bright yellow needles

The technical product consists of hard granules, flakes or bright yellow crystals (depending upon the mode of nitration and drying) and has a melting point of 150 - 160°.

The melting points of alloys of isomeric polynitronaphthalenes, capable of being employed for thermal analysis, are presented in a work by Paskal (Bibl.143).

Table 53 presents the solubilities of α- and β-dinitronaphthalenes in certain solvents. As is evident from the Table, α-dinitronaphthalene dissolves poorly in the common organic solvents, but better in pyridine.

Table 54 presents data on the solubility of dinitronaphthalene in nitric and sulfuric acids.

The specific gravity of technical dinitronaphthalene at 20° is 1.50, and its gravimetric density 0.9 gm/cm³.

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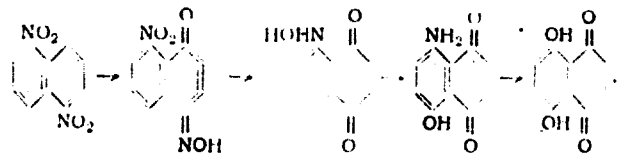
Table 53

Solvent	Temperature of Solution, °C	Solubility, %	
		1,8-dinitro-naphthalene	1,5-dinitro-naphthalene
Dichloroethane	19	2.08	0.45
65% HNO_3	19	0.02	0.01
Chloroform	19	1.37	2.01
Acetone	19	4.59	0.59
Acetone	At boiling	15.98	2.3
Benzene	19	2.01	0.5
Benzene	At boiling	7.44	3.88
Ethyl alcohol (95°)	19	0.04	0.04
Acetic acid	At boiling	2.01	0.43
Carbondisulfide	At boiling	-	insoluble
Absolute ethyl alcohol	22	0.37	0.1
Gasoline	20	0.04	0.02
Water	At boiling	0.07	insoluble
Pyridine	20	-	0.8
Pyridine	At boiling	-	9.1

Upon slow heating to 318°, dinitronaphthalene decomposes with formation of foam. Ignition by a heated wire occurs at 245°.

In strong sulfuric acid, dinitronaphthalene becomes dark due to the formation of naphthazarine (5,8-dioxi-α-naphthaquinone). Formation of this product may take place via the isonitroso compound of nitronaphthoquinone:



These reactions go very slowly with sulfuric acid, but considerably more rapidly in

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Table 54

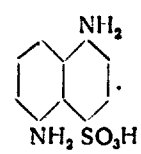
a)	b)				c)
	60	70	80	90	
15,5	—	0,09	0,82	--	—
25,5	0,07	0,14	1,00	13,1	0,05
31,5	—	0,21	1,87	15,05	—
42	—	0,35	—	—	—
48	0,14	0,42	—	—	0,22
55	0,23	0,49	—	—	—
61,5	0,29	0,59	—	—	—
67,5	0,44	...		—	—

a) Temperature, °C; b) Solubility of dinitronaphthalene in %, in nitric acid of various strength, %; c) Percent solubility in 90% H_2SO_4

in the presence of nitric acid. For example, when trinitronaphthalene is subjected to reaction with mixed acid having a high factor of nitrating activity, the consequence is a product having a lower nitrogen content than the initial trinitronaphthalene.

Reaction of nitric acid and zinc with 1,5-dinitronapthalene at 110° results in the formation of β-dioxynaphthoquinone.

At 150°, dilute nitric acid oxidizes 1,5-dinitronaphthalene into the nitro derivatives of phthalic and benzoic acids. Reaction of sodium bisulfite yields 1,5-diaminonaphthalene-sulfonic acid



Sodium sulfite and caustic alkalies have no noticeable effect upon 1,5-dinitronapthalene.

1,8-Dinitronapthalene reacts with sodium sulfite. Its behavior toward acids and

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bases is the same as that of 1,5-dinitronaphthalene. 1,3-Dinitronaphthalene reacts with sodium sulfite, but less ~~xxxxx~~ strongly than does 1,8-dinitronaphthalene. 1,3-Dinitronaphthalene is readily soluble in alcohol. Upon heating, it volatilizes (Bibl.164).

2,4-Dinitronaphthalene may be prepared from 2,4-dinitro-para-toluenesulfono-1-naphthalide without isolation of the intermediate amine (Bibl.165).

1,7-Dinitronaphthalene has been obtained from para-sulfonetoluene-2-naphthylamine dissolving 1 g (50 gm) in hot concentrated acetic acid, and subsequent treatment of the acetic acid (specific gravity 1.42) at 55° (Bibl.166). The resultant product was subjected to diazotization in sulfuric acid. Then, the diazo compound was converted to the 1,7-dinitronaphthalene by heating in alcohol solution.

1,5- and 1,7-Dinitronaphthalene are produced by nitrating β-mononitronaphthalene with mixed acids (Bibl.167).

1,8-Dinitronaphthalene [identical to 1,8-dinitronaphthalene (Bibl.168)] was obtained in the following way: α-naphthaldehyde was converted, with malonic and acetic acid, to ~~α-naphthal~~ α-naphthalmalonic acid, which converted to naphthylacrylic acid. Nitration of the latter, followed by oxidation, yielded, 4,5- or 1,8-dinitronaphthalene.

Nitration of α-mononitronaphthalene by a ~~xxxxxx~~ mixture of nitrosyl sulfuric and nitric acids (solution of SO_2 and HNO_3, specific gravity 1.50) at 20° was performed in a carbontetrachloride medium (in different solvent), as a consequence of which a mixture of 1,3- and 1,5-dinitronaphthalene was obtained (Bibl.169).

Nitration of naphthalene by fuming nitric acid or by mixed acid leads to the formation of dinitronaphthalene (Bibl.170), consisting of a mixture of the 1,5- and ~~xx~~

~~xxx~~

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1,8-isomers.

Dinitronaphthalene is an explosive comparable in strength to dinitrotoluene, but somewhat weaker than the latter (Bibl.171). Its detonation point is 300-310°, its detonation velocity 1150 m/sec (at a density of 1) (Bibl.172), expansion in the Trauzl block is 100 cc, Hess brisance is ~~[illegible]~~ 4 mm at density 0.9, with a detonating cap No.8.

As a consequence of the weak explosive properties and the low sensitivity to detonation, dinitronaphthalene is not employed by itself as an explosive. It enters into the make-up of explosives employed in military engineering and in mining.

A number of formulas containing dinitronaphthalene have been developed and adapted for filling of munitions. A mixture of 48.5% dinitronaphthalene and 51.5% picric acid, called the "Russian mixture", was widely employed during World War I to fill artillery shells of small and medium caliber, and aerial ~~[illegible]~~ bombs. In France, a formula consisting of 20% dinitronaphthalene and 80% picric acid was developed, and it ~~[illegible]~~ came to be known as the "French mixture" (melting point 104°). This mixture was used in France and a number of other countries to fill artillery shells, aerial bombs, and hand grenades. The "Russian mixture" had some advantages for filling purposes because its melting point was 82 - 87°.

Dinitronaphthalene began to be used for military purposes, in mixtures with ammonium nitrate, starting in 1909. ~~[illegible]~~ Mixtures consisting of 88% NH_4NO_3 with 12% dinitronaphthalene, and 80% NH_4NO_3 with 20% dinitronaphthalene, and given the designation ~~[illegible]~~ dinaphthalites (schneiderites) are employed to this day.

In 1934, Favier developed a mixture of 88% NH_4NO_3 and 12% dinitronaphthalene for underground explosive work, as a safer explosive than dynamite.

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Explosives containing various quantities of dinitronaphthalene came into use in all countries.

In the Soviet Union, the following dinaphthalites came into use, starting in 1935. for underground work in mines not dangerous in terms of gas and dust: granular No.1, and pressed No.2, containing 12% and 8.5% dinitronaphthalene respectively.

As a consequence of treatment on crusher rolls, the brisance of granular dinaphthalites is considerably higher than that of the Favier formula (when prepared in the usual manner, the Favier formula has 9 mm brisance and 265 cc fugacity, whereas after treatment on the crusher roll, it has a brisance of 14 - 17 mm and a fugacity of 320 - 340 cc).

Dinaphthalite is one of the powerful ammonium nitrate explosives employed to blast resistant rock. Moreover, of all the ersatz high explosives of the ammonite type, only dinaphthalite satisfies the requirement in terms of emission of toxic gases (50 ltr toxic gas per 1 kg high explosive). This important indicator is of major significance in explosive underta[illegible] in closed [illegible] spaces.

Granular dinaphthalite has a brisance of 15 mm, a fugacity of 320 cc, and is subject to detonation between two cartridges at a distance of 5 mm. The grain size has a major influence upon brisance. The formula having minimum particle size provides greatest brisance and susceptibility to detonation.

When dinaphthalite is treated on roll crushers, the result is a dense mixture of dinitronaphthalene and NH_4NO_3, which also makes for a certain stability to water. This quality makes it possible to employ dinaphthalite in wet face lining.

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In France, dinitronaphthalene is employed in ballistic powders.

Dinitronaphthalene is employed in the aniline dye industry as an intermediate for producing granular brown dye. It is observed that, with increase in the 1,5-dinitronaphthalene isomer, the coloration becomes more stable and of better tint. Moreover, with increase in the 1,5-isomer, a higher yield of dye is achieved.

1,8-Dinitronaphthalene is employed to produce 1,8-naphthylenediamine, which is employed (in the form of its acetyl derivative) in the production of azo dyes.

Trinitronaphthalene. Nitration of 1,5-dinitronaphthalene yields a mixture of the following compositions (in %):

1,3,5-trinitronaphthalene	47.5
1,3,8-trinitronaphthalene	24.0
1,4,5-trinitronaphthalene	9.0

(the residue consisting of impurities).

When nitration of 1,8-dinitronaphthalene, a mixture of the following composition (in %) is obtained:

1,3,8-trinitronaphthalene	85.1
1,4,8-(identical to 1,3,5- and 1,4,5)-trinitronaphthalene	9.4

(the residue consisting of impurities).

Technical trinitronaphthalene is of the following percentage compositions (Bibl.179):

α (1, 3, 5)-trinitronaphthalene	13
β (1, 3, 8)-trinitronaphthalene	54
γ (1, 4, 5)-trinitronaphthalene	8
δ (1, 2, 5)-trinitronaphthalene	23

The isomeric position of technical trinitronaphthalene varies within certain limits in accordance with the conditions of nitration and, correspondingly,

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169 the melting point fluctuates in the range of 110 - 160°. Under given conditions, a mixture of tri- and tetra-nitronaphthalenes is obtained (Bibl.174).

1, 3, 5-Trinitronaphthalene was obtained by Aquiar (Bibl.170) by nitration of 1,5-dinitronaphthalene. 1,3,5-Trinitronaphthalene forms monoclinic crystals melting at 123°, and soluble in acetic acid, chloroform, and alcohol.

1,3,8-Trinitronaphthalene is obtained upon nitration of 1,8-dinitronaphthalene, and crystallizes in the monoclinic form. The melting point is 218°; it is soluble in alcohol, and weakly soluble in ether and chloroform.

1,4,5-Trinitronaphthalene crystallizes in the form of glittering yellow platelets melting at 147°. It dissolves readily in benzene ~~XWXXXX~~ and weakly in ether, alcohol, and chloroform.

1,2,5-Trinitronaphthalene crystallizes in the form of a needle melting at 112 - 113°, and readily soluble in alcohol.

When caustics are reacted with technical trinitronaphthalene, the latter goes into solution weakly, giving the caustic a dark red coloration. An aqueous solution of sodium bisulfite ~~X~~ dissolves trinitronaphthalene in the cold, while upon heating, it converts it to the corresponding nitroaminonaphthalenesulfonic acid.

Sodium sulfite reacts with all isomers of trinitronaphthalene.

At a high temperatures, strong sulfuric acid reacts with trinitronaphthalene, converting it to the solution of dark brown or black color.

In its explosive properties, this product is similar to dinitrobenzene. Table 55 adduces the explosive properties of trinitronaphthalene in mixtures with ammonium nitrate and with other nitro compounds. Upon explosion, trinitronaphthalene liberates 614 ltr/kg of gaseous products, while the heat of explosion is 923 kcal/kg.

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169 Medard showed that the detonation of velocity of trinitronaphthalene may, under certain specific circumstances, exceed 6400 m/sec, and that dinitronaphthalene does not display stable detonation (Bibl.172).

170

Table 55

a)	b)	c)	d) e)	d) f)	g)	h)
	8	307	3,24	—	—	1,52
j)	12	228	2,16	—	5640	1,43
k)	18	406	3,95	7,6	—	1,6 0,74
l)	21	374	—	7,5	—	0,74 Hess' test
m)	4	285	3,11		—	1,55
n)	12	301	3,28			1,55
o)	12	299	3,39	—	—	1,62
p)	12	312	3,72	—	—	1,63

a) Formula; b) Shock sensitivity (weight 10 kg, h = 25 cm), in % explosions;

c) Trauzl fugacity (TAT No.8 cap), cc; d) Brisance (No.8 cap), mm; e) Kast; f) Hess; g) Detonation velocity, m/sec; h) Filling density, gm/cm^3; i) TNT; j) Technical trinitronaphthalene (melting point 150°); k) 16.3% trinitronaphthalene and 83.7% NH_4NO_3; l) 33.[illegible] trinitronaphthalene and 66.4% NH_4NO_3; m) 35% trinitronaphthalene and 65% TNT (freezing point 65°); n) 15% trinitronaphthalene and 85% TNT (freezing point 74°); o) 40% trinitronaphthalene and 60% trinitrophenol (freezing point 82°); p) 20% trinitronaphthalene and 80% trinitrophenol (freezing point 105°)

Table 55 shows that in its fugacity trinitronaphthalene is weaker than TNT by

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170 20 - 25%, in brisance by 25 - 30%, but that its shock sensitivity is XX higher than that of TNT.

Trinitronaphthalene is not produced in significant quantity anywhere. It was employed in Germany as a partial substitute for TNT in the form of an alloy consisting of 67% TNT and 33% trinitronaphthalene, for the filling of shells. Small quantities were employed in France in a mixture of 95% NH_4NO_3 and 5% trinitronaphthalene, for the manufacture of safety explosives. XX

Tetranitronaphthalene. According to A.G.Gorst (Bibl.175), the nitration of 1,8-dinitronaphthalene yields chiefly 1,3,6,8-tetranitronaphthalene, or the β-isomer. Its melting point is 202°. When 1,5-dinitronaphthalene is nitrated, the result consists primarily of two isomers of tetranitronaphthalene: 1,2,5,8- or the δ-isomer, which, upon heating at 270°, decomposes, and the 1,3,5,8-, or γ-isomer, the melting point of which is 194 - 195°. Further, the 1,2,5,8-isomer was also obtained. It decomposes at a temperature of about 300°, without previously having fused. Finally there is the α-isomer the position of the nitro groups in which has not been determined. When it is crystallized out of chloroform, the result is crystals of rhombic form with a melting point of 259°.

When technical trinitronaphthalene is nitrated to tetranitronaphthalene with mixed sulfuric and nitric acids, 110 kcal heat is emitted for every 1 kg of trinitronaphthalene.

171 Davis points out (Bibl.177) that tetranitronaphthalenes are obtained upon the nitration of dinitronaphthalene in the the presence of H_2SO_4 at a temperature of 80°, and an adequate excess of nitric acid. The product yield does not exceed 50%.

Technical tetranitronaphthalene consists of four isomers, and is readily soluble in acetic acid. The acid equilibrium of tetranitronaphthalene somewhat exceeds that of

171 TNT, and therefore, the pure product should not be inferior to TNT in its explosive properties.

Tetranitronaphthalene is not produced anywhere on an industrial scale because of its high cost (large acid consumption).

Nitration of sulfo derivatives of naphthalene. Nitration of the sulfo derivatives of naphthalene does not result in the forcing out (substitution) of the sulfo group by nitro groups as occurs, for example, in the nitration of sulfophenols. In the case of the sulfo derivatives of naphthalene, the nitro groups enter the ring in the meta position with respect to the sulfo groups already present, when nitration occurs.

Lantz (Bibl.178) studied the conditions of nitration of mono-, di- and trisulfonic acids of naphthalene in sulfuric acid solution and found that the most favorable results are obtained when a mixture containing 85 - 90% sulfuric acid is employed. Under optimum conditions of nitration, a maximum of four groups may be introduced into the naphthalene ring (counting the SO_3H already present, and the NO_2 groups entering).

Here it is important to note the fact that the corresponding nitro derivatives of naphthalene cannot be obtained from the naphthalene sulfonic acids in solution, and therefore conveniently, in the technological sense. However, in the production of nitrosulfonic acids, it is desirable first to perform sulfonation, followed by nitration. The performance of nitration immediately after sulfonation makes it possible to employ sulfuric acid in the sulfo batch. Moreover, if the processes were run in reverse order, sulfonation of nitro compounds might result in a small yield of the required compound and in contamination thereof with side products, as a consequence of the ability of

171 nitronaphthalenes to react with strong sulfuric acid.

In the products obtained upon nitration of naphthalene, F.F.Beilstein and A.A.Kurbatow (Bibl.154) discovered phthalic, nitrophthalic and nitrobenzoic acids, nitronaphthols, etc.

With increase in the strength of the mixed acids and the nitration temperature, there is an increase in the intensity of the oxidizing processes, particularly those proceeding with destruction of one benzene ring of the naphthalene.

Section 2. Technology of Nitronaphthalene Production

Production of mononitronaphthalene. Mononitronaphthalene is produced by nitration of naphthalene with mixed sulfuric and nitric acid of various compositions, having an identical factor of nitrating activity (71 - 72 in terms of H_2SO_4). Before nitration, the naphthalene is pulverized (or fused) and first mixed with spent acid from the preceding operation. The run-in time is employed to regulate the rate of heat emission, so as to hold the temperature at 50 - 60°. At the end of run-in, the product is held for 1 hr. The product is separated from the spent acid in the fused state. The product should have a freezing point of not less than 51°, and its yield is 97 - 98% of theoretical. In some cases, the production of technical mononitronaphthalene for the needs of the aniline dye industry special conditions of nitration are developed and a special purification of the product is performed.

Production of dinitronaphthalene. A number of industrial methods of producing dinitronaphthalene are known.

According to Shtettbakher (Bibl.179), it is recommended first that one part mononitronaphthalene be mixed in the nitrator with four parts commercial sulfuric

171 acid of 1.84 specific gravity, whereupon 0.8 of nitro mixture is slowly poured into the contents. The nitro mixture is prepared of equal quantities of strong sulfuric and nitric acids. The dinitronaphthalene, that comes into being in the form of yellow crystals, is separated from the acid on the centrifuge, and is washed with hot water until a neutral reaction is obtained. In the given case, nitration is performed in excess strong acid, which can be utilized only in part, in the first phase of nitration.

172 According to the data of A.A.Scloninia (Bibl.180), Germany had a method of producing dinitronaphthalene by nitration of mononitronaphthalene with strong nitric acid in the cold. Detailed technical information with respect to this method is now available. According to his data (Bibl.180), dinitronaphthalene was made in Germany during World War I by mixing 18 kg mononitronaphthalene and 39 kg sulfuric acid of 1.84 specific gravity, subsequent to which 15 kg strong nitric acid was run in. In course of the nitration process, which lasted for 8 hrs, the batch was periodically agitated. The resultant product was filtered and washed with water. This method is not economical, as it is based on a considerable excess of nitric acid (more than 200%) over the theoretical.

A more profitable process was organized at a plant of the Franco-Russian Society in Shterovka in 1914 - 1917. A mixture of 58% H_2SO_4, 28 - 30% HNO_3, and 22 - 23% H_2O, with a 70% factor of nitrating activity, was employed to produce dinitronaphthalene. Nitration of mononitronaphthalene was performed over a four hour period at 48 - 50°. Twelve parts mononitronaphthalene were run into 44 parts of mixture. After 30 min of holding of the mass in the apparatus, it was cooled to 25 - 30°, and made over for filtration. The product removed from the acids was washed with water in 5% soda solution,

172 and again in cold water, subsequent to which it was washed on the centrifuge and dried at 60 - 70° in a rack dessicator. The spent acid was employed in the first stage of nitration.

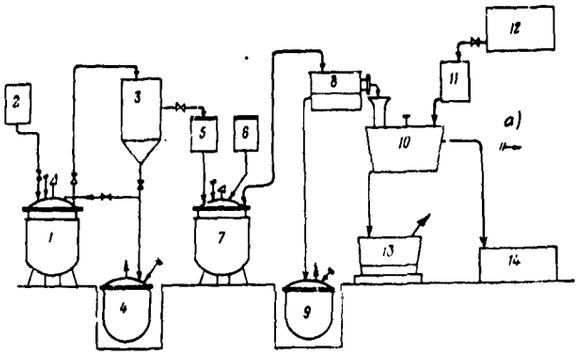

Fig.58 - Method of Producing Dinitronaphthalene

1 and 7 - Nitrators; 2, 5, 6 and 11 - Metering tanks; 3 - Separator; (Suction Filters); 4 and 9 - Rising devices; 8 and 13 - Nutsches; 10 - Washing vat; 12 - Heater; 14 - Trap

a) Compressed air

During World War II, dinitronaphthalene was used in a single stage in Germany (TM 1.181) by nitration of naphthalene with mixed acid of the following composition: 58.5% H_2SO_4; 22.2% HNO_3; 19.3% H_2O. The components were run-in in "inverse" water. The temperature at the time of mixing was held at 34 - 38°, while that at the end of the process was 40 - 50°. Upon completion, the mass was cooled to 30°, and sent on to a filter. Washing was performed first with cold water (6 m^3 per ton dinitronaphthalene), and then with hot water (12 - 14 m^3). Drying was performed at 70 - 80°. The yield of dry products was 80% of the theoretical.

172 The production of dinitronaphthalene in two phases, by a batch process, employing mixed sulfuric and nitric acids as a nitrating agent, is illustrated in the diagram in Fig.58.

According to the diagram, naphthalene is charged into the nitrator (1), where a certain amount of spent acid from the first stage has been left as medium. Run-in is through the hatch, with the agitator operating. Then, nitro mixture is gradually run-in from measuring tank (2), and the nitro mass is held for some time, to permit stirring. Upon completion of the process, the stirrer is stopped, and the nitro mass is permitted to stand, whereupon a portion thereof is forced into separator (3) by compressed air.

173 The entire mononitronaphthalene is forced out of the nitrator. A portion of the spent acid is left in the nitrator, where it serves as medium in which to perform the following operation.

The product tube for delivery of acid and the products into the separator does not reach the bottom of the nitrator. This makes for the maintenance of a constant residue of spent acid in the nitrator for the next first-stage operation.

From separator (3), the mononitronaphthalene that has settled out is sent to metering tank (5) for the second phase, and the spent acid is sent to a settling tank through the pipes (4).

All the nitro mixture to be nitrated is run from measuring tank (6) to nitrator (7), whereupon, the molten mononitronaphthalene is slowly run in, with the agitator operating.

Upon conclusion of the run-in and holding of the nitrator contents, with the agitator

173 operating, it is then sent to the Nutsch (8), with the aid of compressed air. Here the spent acid is squeezed out of the dinitronaphthalene. The spent acid from the Nutsch is sent to settling columns via rising device (9), and the product is raked into the funnel through the side hatch in the Nutsch by means of special rakes. From here it goes, via a wide pipe, to the washing vat (10).

The dinitronaphthalene obtained is washed several times with hot water. The wash water is then sent, by means of an overhead pipe, to a system of traps (14), and then to the drainage system. The hot water for washing comes from heater (12) through metering tank (11). Upon completion of washing, the dinitronaphthalene and the water are lowered over a Nutsch (13), with agitator operating, where the product is squeezed free of water. The pressed dinitronaphthalene is loaded into special cars and sent to drying along a narrow-track railway.

It should be noted that the yield of products both in the first and the second stage are dependent, to a considerable degree, upon the property of the naphthalene employed. The use of pressed naphthalene instead of crystalline naphthalene (which is pure) results in a reduction in the yield in stage one by approximately 5% and in stage two by approximately 3%.

In stage two, the mixture consisting of 74% H_2SO_4 and 15% HNO_3 is employed. The higher percentage of nitric acid facilitates the dumping of the nitro products in the course of nitration. The amount of nitro mixture is determined on the basis of assuring a 40% excess of nitric acid monohydrate over the theoretical. Complete separation of the spent acid from the dinitronaphthalene does not prove possible, and up to 30% goes to the washing vat, along with the dinitronaphthalene.

173 The spent acid from stage two is employed to make up mixed acid for stage one, the factor of nitrating activity of which should be 61 - 62%. The composition of the mixed acid of stage one will vary. For example, a mixture of 45% H_2SO_4, 37% HNO_3, and 18% H_2O will be used, and if the second-stage spent acid and weak nitric acid are completely employed in stage one, the consequence is a mixture containing from 10 - 13% HNO_3 and 56 - 57% H_2SO_4, with a factor of nitrating activity of 61 - 62%.

Nitration is performed in stage one with a gradual rise in temperature to 50° toward the end of run-in of nitro mixture, and with holding at 50° for 1 hr. In the second stage, nitration is performed by running the mononitrotoluene into the mixed acid over a period of 4 hrs, with gradual rise in temperature from 15 - 18° to 40°. This low temperature is required during the run-in time, as a consequence of the tendency of the nitro product to lump at higher temperatures.

The mononitronaphthalene entering a cold, energetically agitated nitro mixture freezes in the form of fine granules. Gradually, starting at the surface, the granules
17% of mononitronaphthalene undergo nitration in depth. The process of nitration proceeds in the solid phase, and its velocity is determined by the rate of diffusion of acid mixture within these granules.

It is particularly important, in the nitration process, to adhere to the temperature conditions, as the lumping of the product depends upon this. Because of lumping it is the formation of a low-melting mixture at a given ratio between
XXX dinitronaphthalene and mononitronaphthalene (40 and 60% respectively).

Table 54 presents the freezing points of alloys of dinitronaphthalene and mononitronaphthalene. Upon achievement of a formula approximating or

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174 equaling the eutectic, the granules of products will begin, if temperature is elevated, to soften and merge into lumps. Table 56 shows that the melting point of a eutectic mixture of pure dry mononitronaphthalene and dinitronaphthalene is 43.5°, and that of the product impregnated with acid is even lower.

Table 56

a)		d)	a)		d)
b)	c)		b)	c)	
0	100	157,3	60	40	43,5
5	95	152,8	80	20	44,4
10	90	148,8	85	15	46,6
15	85	145,2	90	10	48
40	60	123,8	95	5	50,1
50	50	112,5	100	0	53

a) Alloy composition, %; b) Mononitronaphthalene; c) Dinitronaphthalene; d) Freezing point, °C

In practice, there are cases in which the entire product merges into a single viscous mass that adheres to the agitator and the walls of the nitrator. Even a small amount of lumping, leading merely to a little increase in grain size, sharply increases the nitration time and complicates further processing of such a product. The use of mixed acids for the second phase having a nitric acid content of more than 15% makes for lumping of the product inasmuch as nitric acid substantially diminishes the melting point of a eutectic mixture.

Thus, running mononitronaphthalene into mixed acid is terminated at 40°, subsequent to which the temperature is raised to 45°, and the mass is held at this temperature for 1.5 hr.

After the spent acid is separated out, the dinitronaphthalene is washed repeatedly,

174 first with cold, and then with hot water. As a consequence of the fact that nitration results in producing dinitronaphthalene in the form of granules, washing presents serious difficulties. The acid trapped inside the hard granules can only be washed out with great difficulty and it usually takes 10 or 12 washings to reduce the acidity of the product to 0.1%. In addition to a considerable lengthening of the time required for the process of washing, a considerable quantity of waste waters requiring special cleaning.

The washed product is dried by two methods: in chamber driers on racks at 90 - 95°, or, in the same manner as TNT, in the fused condition, at 160 - 180°, in drying baths. Drying is followed by flaking. In this situation, the product is produced in the form of fine flakes.

Production of trinitronaphthalene. A number of investigators have concerned themselves with the manufacture of trinitronaphthalene.

175 Patard (Bibl.159) has nitrated naphthalene with mixed acids of various compositions at 110°. He has found groups of nitro mixtures of various compositions capable of nitrating naphthalene to specific degrees of nitration. A.V.Sapozhnikov (Bibl.176), who elaborated on Patard's material, showed that trinitration of naphthalene can be carried out by mixed acids containing not more than 50 molar and not less than 25 molar percent H_2O. When the mixed acids are stronger than this, the result is, at first, tetranitronaphthalene at up to 20% molar H_2O, followed by the possibility of partial carbonization.

Friendler (Bibl.182) produced trinitronaphthalene by direct nitration of mononitronaphthalene.

A.A.Solonina (Bibl.180) provides a recipe for producing trinitronaphthalene,

175 employed at the Okhta Powder Works, under which 11 kg mononitronaphthalenes are mixed with 39 kg sodium nitrate, the mixture is rubbed through a sieve, introduced into the reactor, to which 102 kg commercial sulfuric acid is added. This method was developed by A.V.Stepanov (Bibl.153). Its chief shortcoming is the impossibility of utilizing spent acid, as this sharply increases the cost of the product.

Aguiar (Bibl.170) produced trinitronaphthalene from dinitronaphthalene. To do this, 100 gm 1,5-dinitronaphthalene was mixed with 1000 gm strong nitric acid at 120 - 130° for one hour in a reactor with a reflux condenser. The result of the reaction was the production of 1,3,5-trinitronaphthalene.

F. Trinitrophenol and Other Nitro Derivatives of the Phenols

Trinitrophenol was first obtained in 1771 by Woulff by reacting nitric acid and indigo (Bibl.183). Because of its acid properties and bitter taste (Πικρος - meaning bitter) was called picric acid. In 1813, the same product was obtained by Loran, by the nitration of phenol. The comparatively accessible initial raw material made it possible to organize the manufacture of picric acid, which was employed as a yellow dye for wool and silk. At that time, the explosive nature of picric acid was not known.

In 1868 - 1869 it was proposed to employ the potassium and ammonia salts of picric acid as a component of explosives made from potassium nitrate. In 1873 Sprengel discovered that picric acid could be exploded by the use of a mercury fulminate detonating cap. This made it possible to employ it independently to fill artillery shells. It was found that, to explode cast picric acid, one needed an intermediate detonator of pressed picric acid, which in turn would dependably detonate due to the action of a mercury fulminate detonating cap.

Starting in 1886, picric acid came to be employed widely to fill shells in

174 France under the designation of Melinite, starting in 1888 in England under the designation Lyddite, in Japan under the title of Shimose, in Germany under the designation C/88 and in Russia, starting in 1896, under the designation Melinite.

Thanks to the fact that picric acid was the first explosive which, having high power and brisance, was less dangerous to store and to handle than the black powders hitherto known in military practice, nitroglycerin and pyroxylin, its manufacture immediately was undertaken on a very large scale.

In Russia, the manufacture of picric acid was first undertaken in 1896 at the Okhta Works (which burned in 1907) and somewhat later, during World War I, at three other plants. At two plants, picric acid was manufactured from phenol, and at the third from benzene, through dinitrochlorobenzene as intermediate (Bibl.184).

176 Toward the end of World War I, about 10,000 tons of picric acid was being manufactured per year in Russia, 25,000 tons in Germany, and about 50,000 tons per year each in Britain and France.

However, the scale of production of picric acid, even at the beginning of the Twentieth Century, began to diminish, as a consequence of its negative properties such as reaction with the shell casing, resulting in the formation of iron picrate, highly sensitive to shock, and the fact that it could not be employed to ammonites.

At the present time, TNT has replaced picric acid almost in its entirety, and its production in peace time has been sharply reduced. In wartime, the significance of picric acid as an explosive remains. This is testified to, in part, by investigations in the field of rationalization of existing methods, as well as the development of new methods of producing picric acid. Particularly great

176 attention has been given, in recent years, to producing picric acid directly from benzene, by the method of oxidizing nitration.

During World War II, a number of major scientists worked on the problem of a more profitable method of producing picric acid, to wit, by oxidizing nitration of benzene in the presence of a mercury catalyst. These scientists included N.G.Laptev and A.I.Titov (Bibl.185), and in the USA Dunning, Robertson, Westheimer, etc. (Bibl.186, 187).

In the course of World War II, 33,000 tons of picric acid was manufactured in Germany. In Japan, according to the data of Colley (Bibl.188), picric acid production was on a rather substantial scale.

Section 1. The Chemistry of the Production of Phenol Nitro Derivatives

Nitro derivatives of phenol and, in particular, trinitrophenol, are produced in industrial practice from phenol or benzene (via dinitrochlorobenzene as intermediate, or the nitration of benzene in the presence of mercury nitrate). Each of these methods enjoys certain advantages. In peacetime, they permit the manufacture of highly valuable intermediates in the form of dinitrophenol and dinitrochlorobenzene, which are widely employed in the manufacture of dyes.

a) Production of Trinitrophenol from Phenol

Phenol C_6H_5OH is a crystalline substance, colorless or pinkish, with a freezing point of 42.5° and boiling point of 182°. The specific gravity of phenol at 50° is 1.0466. Its thermal capacity is 0.561 kcal/kg/°C, and its latent heat of vaporization at the boiling point is 114 kcal/kg. The temperature of autocombustion of the fumes in air is 430°.

176 Phenol constitutes from 10 - 25% of coal tar. The large demand for phenol on the part of a number of branches of the chemical industry (plastics, aniline dye, lacquer and paint, etc.) gave rise to the need for large-scale production of synthetic phenol.

Modern methods of phenol synthesis employed benzene as the starting substance. Phenol is produced in the following ways.

1. By fusing the sodium salt of benzenesulfonic acid with caustic, the principal stages of the process being:

a) sulfonation of benzene

$$C_6H_6 + H_2SO_4 \rightarrow C_6H_5SO_3H + H_2O;$$

b) formation of the sodium salt of benzenesulfonic acid

$$2C_6H_5SO_3H + Na_2SO_3 \rightarrow 2C_6H_5SO_3Na + SO_2 + H_2O;$$

c) fusing of the sodium salt of benzenesulfonic acid with caustic soda:

$$C_6H_5SO_3Na + 2NaOH \rightarrow C_6H_5ONa + Na_2SO_3 + H_2O;$$

d) decomposition of the phenolate

$$2C_6H_5ONa + SO_2 + H_2O \rightarrow 2C_6H_5OH + Na_2SO_3.$$

177 2. Hydrolysis of chlorobenzene by caustic, in accordance with the reaction

$$C_6H_5Cl + 2NaOH \rightarrow C_6H_5ONa + NaCl + H_2O.$$

With subsequent decomposition of the sodium phenolate by acid (sulfuric or hydrochloric)

$$C_6H_5ONa + HCl \rightarrow C_6H_5OH + NaCl.$$

Hydrolysis is performed with a 10% aqueous caustic soda solution at 200 - 250 atm pressure and 300 - 350°.

3. Catalytic hydrolysis of chlorobenzene by steam. Hydrolysis of chlorobenzene by steam

$$C_6H_5Cl + H_2O \rightarrow C_6H_5OH + HCl$$

177 is performed at 450 - 500° over a catalyst (silica gel and others).

4. Decomposition of hydrogen peroxide of isopropylbenzene. Under this method, two valuable products, phenol and acetone, are obtained simultaneously. The process is run in stages:

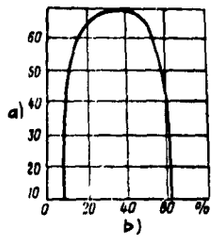
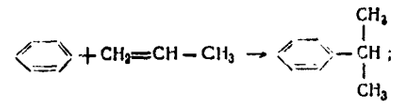
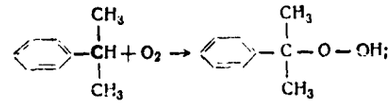


Fig.59 - Effect of Temperature upon Solubility of Phenol in Water
a) Temperature, in °C;
b) Solubility of Phenol

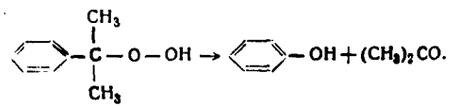
a) production of isopropylbenzene (cumene) by alkylation of benzene by propylene:



b) oxidation of isopropylbenzene by air (in an aqueous alkaline emulsion under pressure at 130°) with conversion (as the consequence of a chain reaction) into the hydrogen peroxide



c) Decomposition of the hydrogen peroxide isopropylbenzene (by boiling in dilute sulfuric acid under pressure) into phenol and acetone:



Synthetic and coal-derived phenols contain cresols and other impurities. Phenol designed to yield trinitrophenol should be a colorless or slightly pink crystalline product with a freezing point at not less than 37°.

Phenol and water are mutually satisfactorily soluble (Fig.59). The critical temperature of solution is 68.3° above which phenol and water will mix in any ratios. Upon long contact with the air, phenol, undergoing oxidation, acquires a reddish tint,

177 and, upon absorption of moisture from the air, liquifies.

Phenol is weakly acid, and, upon reaction with bases, yields salts called phenolates. Thus, for example, it dissolves readily in aqueous solutions of caustic soda and caustic potash with formulation of phenolate in accordance with the following equation

$$C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O.$$

Phenol does not react with soda.

In working with phenol, it must be borne in mind that it is highly poisonous and moreover, tends to eat away the skin upon contact, and causes ulcers that heal with difficulty.

Phenol is considerably more reactive than benzene and toluene. It undergoes sulfonation and nitrates readily. Nitration with weak nitric acid is an autocatalytic process and is caused by the formation of nitrous acid as the product of secondary reaction (Bibl.189).

178 When phenol is nitrated with nitric acid, a mixture of ortho- and para-nitrophenols results. The temperature at which nitration occurs affects the composition of the nitrophenols, and increase in temperature increases yield of the ortho-isomer(Bibl.190). The reaction goes analogously when a mixture of sodium or potassium nitrate and dilute sulfuric acid is employed for nitration (Bibl.191). Meta-nitrophenol does not come into being upon direct nitration of phenol, and its production is usually from meta-nitroaniline via the diazo compound.

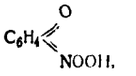
Table 57 presents certain properties of nitrophenols.

As we see from Table 57, ortho-nitrophenol differs from the meta- and para-nitrophenols by the coloration of the crystals and the sharp odor. Moreover,

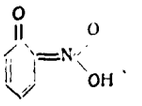
Table 57

Chemical	Melting Point, °C	Boiling Point, °C	Appearance
Ortho-nitrophenol	45	214.5	Yellow crystals having a sharp odor similar to that of nitrobenzene
Meta-nitrophenol	96	194 at 70 mm Hg (with sublimation)	Colorless, odorless crystals
Para-nitrophenol	114	-	Colorless crystals, but a solution in alkali is colored yellow

as distinct from other isomers, it is readily distillable by steam. The cause of the coloration, according to Hantsch, is the tendency of ortho-nitrophenols to form aci forms:



having a quinoid structure



Phenols can be nitrated directly only by highly dilute acids. This is difficult and unprofitable from the technical point of view. Nitration of phenol by a mixed acid even of middle strength (total acidity 70 - 75%) is, however, virtually impossible, as the high reaction velocity and, as a consequence, the rapid liberation of heat results in oxidation and resinification. To prevent these processes from taking place, the phenol is first sulfonated, to yield a less reactive compound - phenol sulfonic acid. Moreover, the nitration of the latter results in a lesser thermal effect than the direct nitration of phenol.

Sulfonation of phenol. When phenol is acted upon by sulfuric acid, one, two, and sometimes three hydrogen atoms of the sulfo group may be replaced in its molecule. The

178 number of entering sulfo groups depends primarily upon the strength and amount of acid and, to a lesser degree, upon the temperature and reaction time.

In accordance with the reaction equation

$$C_6H_5OH + H_2SO_4 \rightleftarrows C_6H_4(OH)(SO_3H) + H_2O$$

the sulfonation process is accompanied by the formation of water, which dilutes the sulfuric acid and, moreover, is reversible (Bibl.192). In accordance with the most recent studies (Bibl.193), the active sulfonating agent in aqueous sulfuric

179 acid is the monomer of sulfuric anhydride (SO_3) or, possibly, the sulfate solvate thereof, and, in oleum, also the dimer of sulfur trioxide (S_2O_6) which is present there in the form of the solvate of trisulfuric acid.

These particles are formed in accordance with the following equations:

$$2H_2SO_4 \rightleftarrows S'O_3 + H_3O^{\oplus} + HSO_4^{\ominus};$$
$$4H_2SO_4 \rightleftarrows S_2O_6 + 2H_3O^{\oplus} + 2HSO_4^{\ominus}.$$

Sulfonation apparently goes in a manner similar to that of nitration, in two stages:

$$ArH + SO_3 \rightleftarrows Ar^{\oplus}\begin{matrix} H \\ SO_3^{\ominus} \end{matrix};$$

$$Ar^{\oplus}\begin{matrix} H \\ SO_3^{\ominus} \end{matrix} \rightarrow Ar^{\oplus}SO_3^{\ominus} + H^{\oplus}.$$

Melander (Bibl.194) found that, as distinct from nitration, sulfation is accompanied by a noticeable hydrogen isotope effect: in the sulfation of benzene or bromobenzene containing tritium, the proton is displaced by weak oleum somewhat more rapidly than is the tritium. This testifies to the fact that the second stage is quite slow as compared to the inverse direction of the first stage.

The velocity constants of the reactions of sulfonation and hydrolysis, and as a

179 consequence thereof, the equilibrium constants depend upon the strength of the sulfuric acid (Bibl.195).

With reduction in the strength of the sulfuric acid, the sulfonation velocity constant diminishes, and the velocity constant of hydrolysis increases, although in less marked fashion. In this case, the equilibrium constant also diminishes. As a consequence of the significant diminution in the sulfonation velocity constant, the reaction virtually ceases at a particular concentration of the sulfonating agent. This strength of sulfuric acid, expressed in per cent of SO_3, has come to be denoted as the π of sulfonation.

The value of the π of sulfonation depends upon the nature of the compound being sulfonated, upon the temperature and degree of sulfonation, i.e., upon the number of sulfo groups entering.

The quantity of sulfuric acid or oleum x (in kg), required for monosulfonation of p kg of organic substance with a molecular weight of M, may be computed on the equation

$$x = \frac{80(100-\pi)\cdot p}{(S-\pi)\cdot M},$$

where S is the total concentration of SO_3 in the initial sulfonating agent. It is clear from the formula, that the higher the concentration of SO_3 in the initial sulfonating agent, the lower the quantity thereof required for sulfonation.

The π of sulfonation may be reduced by increasing the reaction time and, particularly, by increasing the sulfo acids content of the reaction mass. These, undergoing hydration, are bound by the water of reaction (Bibl.196).

For the monosulfonation of phenol, π = 55% SO_3, for disulfonation, it is 68% SO_3, and for trisulfonation it is 81.6% SO_3. In all three cases, the temperature at which

179 the material is held has to be 120° (Bibl.197).

In choosing the strength of the sulfonating agent and the temperature of sulfonation, one must take into consideration the possibility that side processes will occur. The employment of a sulfonating agent of high strength (containing free SO_3) may result in the formation of sulfones:

$$ArSO_3H + HAr \rightarrow ArSO_2Ar + H_2O.$$

180 the obtaining of which is facilitated by the presence of the sulfonic acid, which is already quite considerable in quantity, and by high temperature.

The high temperature of sulfonation may also induce oxidation. This is facilitated by certain XXX catalysts such as Hg and Se (Bibl.198). In sulfonation, the oxidizing effect is manifested both in the formation of oxy compounds, and in far-reaching changes that may include the combustion of organic substances.

The temperature at which the sulfonation process occurs XX affects the position of the sulfo group entering the compound. When sulfonation occurs in the cold, the sulfo group enters in the ortho position. When it occurs at 100°, the sulfo group enters in the para position. The heating of ortho-phenolsulfonic X oxide at 100° converts it to para-phenolsulfonic oxide. This fact is made use of in production of picric acid. Inasmuch as para-phenolsulfonic oxide nitrates at [redacted] higher speed than ortho-phenolsulfonic oxide (Bibl.199), as a consequence, when phenol is sulfated, the sulfo mass is held at 100 - 110° when the process comes to an end, for the purpose of converting ortho-phenolsulfonic acid into para-phenolsulfonic acid.

The heat effect of reaction of sulfonation of aromatic compounds is less than the effect of the nitration reaction. From this, we are able to understand the reversible nature of the sulfonation reaction, and the mutual [redacted] convertibility of the

180 isomers of the sulfonic acids, as well as the possibility of ready substitution of the sulfo groups by the nitro groups.

The isomerization of the sulfonic acid is explained by the fact that the ortho-isomer is less stable to hydrolysis than the para-isomer. However, inasmuch as the rate of sulfonation is high in the ortho-position, when temperature is [illegible] primarily this isomer that is formed. When temperature rises, the ortho-isomer undergoes hydrolysis, and the para-isomer is simultaneously formed. Under these circumstances, it does not undergo hydrolysis (Bibl.195).

Tables 58 and 59 illustrate the effect of the strength of the sulfuric acid, [illegible] the length of [illegible] sulfonation time, and of temperature, upon the yield of phenoldisulfonic acids. In [illegible] all the experiments, 5 parts sulfuric acid by weight are taken per part of phenol by weight (Bibl.200).

Table 58

Percentage Strength of H_2SO_4	92	93	94	96	97	100
Yield of disulfonic acid per hr at 100°, %	62	66	71	82	91	100

Table 59

Time, hrs	Percentage Yield of Phenol Disulfonic Acid when Reacted with 93% H_2SO_4, at °C		
	75	100	150
0,25	--	48	50
0,5	51	65	66
1,0	59	66	66,5
2,0	—	68	—
4,0	—	68,5	—

It is evident from the data adduced that the best conditions for producing [illegible] phenoldisulfonic acid are a temperature approximating 100°, and a sulfonation time [illegible] of about 30 min.

180 An increase in the temperature to 150° has virtually no effect upon the yield of disulfonic phenol, but, at the same time, it results in the formation of sulfones. (Bibl.201).

When phenol is heated with ten times the quantity of 20% oleum at 120° for three hours, a mixture of the di- and trisulfonic acids of phenol is produced (Bibl.202). The sulfonation of phenol by 20% oleum results in the formation of 2,4- and 2,6-

181 disulfonicphenol and partially, of trisulfonicphenol. 2,6-Disulfonicphenol readily isomerizes at 100 - 110° to 2,4-disulfonicphenol. Therefore, in the manufacturing process, when sulfonation of phenol comes to an end, it is held at 100 - 110°, with the object of converting the 2,6-disulfonicphenol to the 2,4-isomer, which then undergoes freer nitration.

The sulfo derivatives of phenol usually are not separated from the sulfo mass, but undergo direct nitration.

In the pure form, the sulfo oxides of phenol are colorless crystals, which acquire a reddish tint in air. They have no characteristic melting and boiling points, and, when heated, decompose with carbonization. Sulfonic acids readily dissolve in water. They are strong acids and form two types of salts: sulfonates, in which the hydrogen of the sulfo group is replaced by a metal, and phenolates, in which the hydrogen of the hydroxyl group is replaced by a metal.

The sulfo group is readily neutralized even by carbonates. However, the hydroxyl group in the monosulfonic acids is neutralized with difficulty by carbonates.

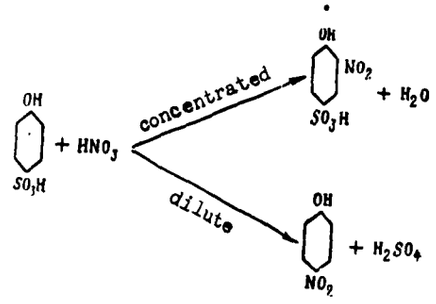
The acid properties of the sulfonic acids of phenol increase in the following sequence: meta-, para-, ortho-phenoldisulfonic acids. Their susceptibility to hydrolysis diminishes in the same order.

181 Nitration of sulfonicphenol. This process goes considerably more quietly than the nitration of phenol, and is capable of being affected by mixed sulfuric and nitric acid. The stability of phenol with respect to oxidizers increases when electrically negative groups are present in the molecule. Therefore, when the degree of sulfonation of phenol is increased, the yield of nitro derivatives rises, and the intensity of the oxidizing processes diminishes.(Bibl.197, 200).

In dilute sulfuric acid, nitric acid exercises an oxidizing effect at elevated temperature, as a consequence of which oxalic acid is formed. Oxidation goes the more noticeably, the less the degree to which the phenol ring is protected by substituting groups.

King has shown (Bibl.199), that, when nitric acid acts upon phenolsulfonic acid in the presence of excess strong sulfuric acid, the hydrogen in the ring is replaced by a nitro group. In the presence of dilute sulfuric acid, the sulfo group is replaced by nitro groups.

The introduction of the nitro group may be expressed by the following diagrams:



Consequently, when three nitro groups are introduced into the phenol molecule, the most advisable procedure is to employ these regularities of the process in the following order:

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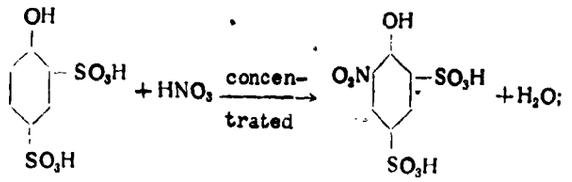

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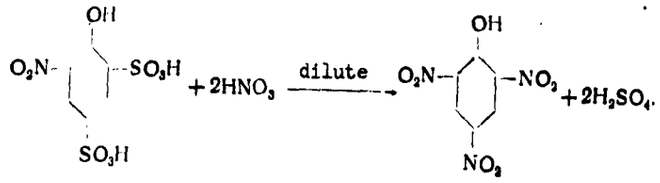


In this case, no acid circulation is required in the production of picric acid from phenoldisulfonic acid. The most concentrated mixed acid is required at the beginning of the process for the purpose of introducing the first nitro group. Subsequently, the nitro mixture is diluted by water as a reaction product, rendering the medium more favorable to substitution of a nitro group for the sulfo group. If the nitration process is properly set up, it will go under the most favorable circumstances: a homogeneous medium, thanks to the good solubility of sulfonic acids and their nitro derivatives in sulfuric acid. At the end of the process, crystals of a considerably more difficultly-soluble trinitrophenol will come down.

Disulfophenol nitrates at a lower rate than does phenol, and is more stable with respect to oxidizing processes. Nevertheless, oxidation does occur upon nitration. To reduce it, the temperature is held at not over 60°, in the introduction of the first nitro group.

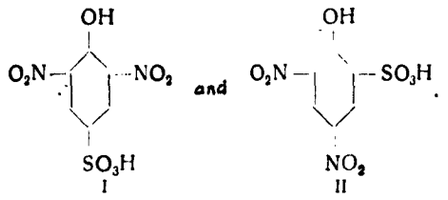
In the first stage of nitration, upon addition of 1 mole HNO_3 to mole of disulfonic phenol, nitrodisulfonicphenol is formed:

$$C_6H_3(SO_3H)_2OH + HNO_3 \rightarrow C_6H_2(NO_2)(SO_3H)_2OH + H_2O.$$

The [illegible] 6-nitro-2,4-disulfonicphenol isomer is produced, as the bulk of

182 the sulfonicphenol consists of 2,4-disulfonicphenol. A certain quantity of 4-nitro-2,6-disulfonicphenol is also formed from the 2,6-disulfonicphenol present in the sulfo mass.

The effect of the second molecule of HNO_3, is that the SO_3H group is replaced by an NO_2 group, and the two following isomers of dinitrosulphonic phenol result:



Both these isomers are formed from 6-nitro-2,4-disulfonicphenol, the former isomer predominating. However, the 4-nitro-2,6-disulfonicphenol isomer yields only 4,6-dinitro-2-sulfonicphenol. The formation of 4,6-dinitro-2-sulfonicphenol is undesirable, as its further nitration goes only with difficulty. This is not to be avoided completely, but the quantity diminishes as a consequence of conversion of 2,6-disulfonicphenol into 2,4-disulfonicphenol by holding the sulfo mass at 100 - 110° for some period.

With further nitration, both isomers of dinitro-sulfonicphenol converts to picric acid, in accordance with the equation:

$$C_6H_2(NO_2)_2(SO_3H)\,OH + HNO_3 \rightarrow C_6H_2(NO_2)_3OH + H_2SO_4.$$

The second nitro group enters at 60 - 80°, and upon the introduction of the third nitro group, the temperature rises to 100°. The mixture is held at the same temperature. The high temperature of the nitration process results in a considerable

183 oxidation of nitrophenols to oxalic acid, which increases the consumption of nitric acid by 20 - 25%, and substantially reduces the yield of nitro products.

The need to perform nitration at high temperature is induced by the difficulty

183 in converting 4,6-dinitrophenol-2-sulfonic acid to the trinitroderivative. The incompleted denitrated product reduces the yield of picric acid and reduces its quality, inasmuch as it is not possible to separate it completely from the nitric acid by washing with water.

In the production of nitro compounds, it is desirable to replace oleum by commercial sulfuric acid, as this makes it possible to set up a closed acid circulation. After regeneration, the spent acid is reconverted to commercial sulfuric acid, which may again be used for sulfonation of the phenol. In connection therewith, a process for the production of picric acid without oleum was investigated, consisting of the following: sulfonation is carried out by adding 91 - 91.3% commercial sulfuric acid to the molten phenol at 40°, in a period of 5 - 7 min. The temperature rises at first as a consequence of the heating reaction, and is then brought to 100 or 110° on an oil bath, and allowed to stand at that level. The resultant sulfonicphenol, consisting of a mixture of mono and disulfonic derivatives, the composition of which is indicated in Table 60, is nitrated by melange to trinitrophenol.

Table 60

a)		1	2	3	4	5	6	7	8	9
b)		10	10	20	20	30	30	40	40	60
c)	mono-	74,7	44,4	—	43,5	58,0	44,2	57,3	40,7	—
	di-	25,3	55,6	—	56,5	42,0	55,8	42,4	59,3	—
d)	mono-	—	33,5	—	29,9	—	30,8	—	—	28,6
	di-	—	66,5	—	70,1	—	69,2	—	—	71,4

Note. In experiments 1,3,5, and 7, the temperature maintained was 100°, and in experiments 2,4,6,8, and 9, was 110°.

a) Experiment number; b) Holding time, min; c) Composition of the sulfonicphenol, in %, at a 1:5.4 ratio of phenol to sulfuric acid; d) Percentage composition of sulfonicphenol at 1:7.5 ratio of phenol to sulfuric acid

183 In order to hold constant the amount of sulfuric acid produced in nitration, and thereby to eliminate the effect of other factors upon the yield of picric acid, the sulfonicphenol produced is diluted in the cold by commercial sulfuric acid. After nitration, the spent acid contains 77.8% sulfuric acid. XX Under these conditions, the yield of picric acid, regardless of the degree of sulfonation, is identical, and comes to 83 - 84% of the theoretical. Consequently, the nitrability of monosulfonicphenol upon identical acidity of the medium is the same as that of disulfonicphenol. This circumstance compels one to assume that the factor influencing the yield of picric acid is not so much the degree of sulfonation as the strength of the nitrating mixture. Consequently, XX in the production of picric acid, oleum may be replaced by commercial sulfuric acid, if we take the ratio of phenol to sulfuric acid monohydrate as 1:7.5. This does not require the dilution of the sulfo mass by commercial sulfuric acid, as is the case in sulfonation with oleum.XX

b) Production of Trinitrophenol from Benzene via Dinitrochlorobenzene

The production of trinitrophenol from benzene requires several stages, XXXXXXXX in accordance with the following equations.

1. Chlorination of benzene to chlorobenzene:

$$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl.$$

184 When benzene is chlorinated, the result is not only monochlorobenzene but polychlorides. There is also a part of the benzene that does not go into the chlorination reaction, and therefore the liquid obtained in chlorination is to be divided by distillation, in order to emerge with comparatively pure monochlorobenzene.

2. Nitration of monochlorobenzene to dinitrochlorobenzene by fixed sulfuric and nitric acid:

$$C_6H_5Cl + 2HNO_3 \xrightarrow{H_2SO_4} C_6H_3(NO_2)_2Cl + 2H_2O.$$

184 3. Saponification of dinitrochlorobenzene to sodium dinitrophenolate:

$$C_6H_3(NO_2)_2Cl + 2NaOH \rightarrow C_6H_3(NO_2)_2ONa + H_2O + NaCl.$$

4. Production of dinitrophenol by treatment of sodium dinitrophenolate by sulfuric acid:

$$2C_6H_3(NO_2)_2ONa + H_2SO_4 \rightarrow 2C_6H_3(NO_2)_2OH + Na_2SO_4.$$

5. Nitration of dinitrophenol to trinitrophenol by mixed sulfuric and nitric acid:

$$C_6H_3(NO_2)_2OH + HNO_3 \xrightarrow{H_2SO_4} C_6H_2(NO_2)_3OH + H_2O + 12{,}9 \text{ Kcal / mole}$$

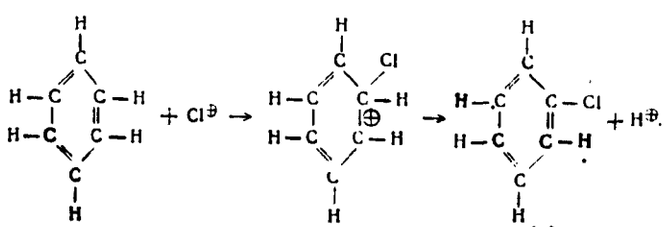
The polychlorides obtained as by-products in the chlorination of benzene are purified and employed for the production of dyes, and the hydrogen chloride liberated is trapped by water and used to produce hydrochloric acid. Chlorination of benzene is performed by gaseous chlorine in the presence of a catalyst - iron chloride, the strength of which in the benzene should be 0.01 - 0.015%. The iron chloride, [illegible] may either be introduced [illegible] into the benzene delivered to chlorination or produced directly in the reactor. To accomplish the latter, iron is placed in the reactor, and is converted to $FeCl_3$:

$$2Fe + 3Cl_2 \rightarrow 2FeCl_3.$$

In accordance with modern concepts, the catalyst promotes the formation of positively charged ions of chloride in accordance with the following mechanism (Bibl.203)

$$FeCl_3 + Cl_2 \rightleftarrows FeCl_4^{\ominus} + Cl^{\oplus}.$$

The $Cl^{\oplus}$ ion reacts subsequently with the aromatic compounds:



184 The proton reacts with $FeCl_4^-$, recovering the catalytically active salt $FeCl_3$, and forming hydrogen chloride:

$$FeCl_4^{\ominus} + H^{\oplus} \rightleftarrows FeCl_3 + HCl.$$

In accordance with the mechanism presented, the catalyst acts only upon the chlorine. However, the action of the catalyst upon the aromatic compound is also possible. This is testified to, in part, by the effect of the nature of the catalyst upon the ratio between the chlorine derivative isomers.

185 When benzene is chlorinated in the presence of iron chloride, the process goes in the direction of formation of chlorobenzene only at the very beginning:

$$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl,$$

but later, the chlorobenzene formed converts to dichlorobenzene:

$$C_6H_5Cl + Cl_2 \rightarrow C_6H_4Cl_2 + HCl.$$

The yield of chlorobenzene (in terms of benzene) approximates 100% at the onset of chlorination. As the reaction progresses, it continually declines, inasmuch as, as the con entration of chlorobenzene increases, the rate of conversion thereof into dichlorobenzene becomes greater than the rate of formation.

To avoid the formation of a large quantity of polychlorides, it is desirable to stop the chlorination reaction when the concentration of chlorobenzene attains 32 - 50%. In this situation, the polychlorides formed constitute not more than 5% of the resultant monochlorobenzene by weight.

The chlorination reaction is monitored by determining the specific gravity of the reaction mixture.

The temperature of chlorination influences the formation of polychlorides. The temperature coefficient of the chlorination rate of benzene is 8 or 9% lower than that

185 of chlorobenzene. Therefore, with increase in temperature of chlorination, more polychlorides are formed.

Previously, the chlorination process was carried out by a batch-wise method at 20 - 25°. Today, chlorination is performed by a continuous method at the boiling point of the reaction mixture (76 - 83°). This makes for intensive loss of heat of reaction due to partial evaporation of benzene and chlorobenzene from the boiling mass. Inasmuch as the chlorination reaction is exothermic (about 28 kcal are released per mole of chlorine), the output rate of chlorators depends, for all practical purposes, upon the rate at which heated reaction is removed. Therefore, chlorators MX that function under conditions of boiling of the reaction mixture show a higher rate of output than the ordinary type.

For purposes of chlorination, the benzene and chlorine should be as dry as possible, as the hydrogen chloride formed in reaction, upon dissolving in water, rapidly decomposes the catalyst and the apparatus.

Drying of the benzene is usually performed by means of azeotropic distillation, and drying of the chlorine by passing it through sulfuric acid.

Chlorobenzene is separated from the chlorinated benzene by distillation, which presents no great difficulties in view of the great difference in the boiling point of the components, constituting chlorinated benzene: 80.4° for benzene, 132° for chlorobenzene, and 172 - 180° for polychlorides. Prior to distillation, the chlorinated benzene is treated with dry soda or limestone, followed by filtration. This is necessary in order to remove hydrogen chloride, which may induce corrosion.

Chlorobenzene (monochlorobenzene) consists of a colorless, mobile liquid smelling of almonds. It is not soluble in water, but dissolves well in alcohol, ether, benzene,

185 chloroform, and carbondisulfide. The boiling point of chlorobenzene is 132.2°; the freezing point is 45.2°; specific gravity is 1.106 gm/cm^3 at 25°. The temperature is 0.31 kcal/kg/°C. Chlorobenzene is hot, and emits hydrogen chloride when heated.

Its chemical activity is lower than that of the halide-substituted hydrocarbons of the aliphatic series. Chlorobenzene reacts with ammonia only when heated in an autoclave to 180 - 200° in the presence of copper salts or pulverized copper. Strong aqueous solutions of caustics cleave chlorine away from chlorobenzene only at 300°. The strength of the bond between the halide and the ring is diminished upon introduction of NO_2 and the COOH group into the ring. Chlorine is activated with particularly high degree by these groups which are in the ortho-

186 and para-position with respect thereto. Chlorobenzene is slightly narcotic.

Table 61 presents some of the physical properties of the polychlorides, which are also produced in the chlorination of benzene.

Table 61

a)	b)	c)	d)
1,4 -dichlorobenzene (para-)	52,69—53,2	171—174	at 20°—1,3581
1,2-dichlorobenzene (ortho)	14	179	at 19°—1,3039
1,3-dichlorobenzene (meta-)	e)	—	at 25°—1,2835
1,2,3-trichlorobenzene	53—54	212—219	—
1,2,4-trichlorobenzene	17	205—213	at 10°—1,574
1,3,5-trichlorobenzene	53,4	208,5	—
1,2,3,4-tetrachlorobenzene	45—46	254	—
1,2,3,5-tetrachlorobenzene	50—51	246	—
1,2,4,5-tetrachlorobenzene	137—138	236—246	at 175°—1,3958
Pentachlorobenzene	84—86	275—276	at 81°—1,6095
Hexachlorobenzene	222,5	322—332	at 203°—1,519

a) Isomers; b) Melting point, °C; c) Boiling point, °C; d) Specific gravity; e) Freezes in a mixture of water and ice

Nitration of chlorobenzene to dinitrochlorobenzene goes in two stages. First, the first nitro group is introduced at a temperature of 45 - 50°. The result of

nitration is a mixture of ortho-, para-, and meta-nitrochlorobenzene. The formation of the meta-isomers is undesirable, as upon further nitration, it converts to asymmetrical trinitrophenol. The yield of meta-isomer depends upon temperature. The higher the temperature of nitration, the higher the yield of meta-isomer. Certain of the physical properties of nitrochlorobenzene are presented in Table 62.

Table 62

a)	b)	c)	d)
Freezing point, in °C	32,5	46,0	83,0
Boiling point, in °C	245	235	242

a) Nitrochlorobenzene isomers; b) Ortho-; c) Meta-; d) Para-

Nitrochlorobenzene is subjected to further nitration to dinitrochlorobenzene at 75 - 80°. 2,4-dinitrochlorobenzene (or α-) is a virtually colorless crystalline substance with a freezing point of 53.4°. The 2,6- or β-isomer freezes at 43.2°, and the 3,5-, or γ-isomer, at 27°. The technical product consisting chiefly of α-isomer has a freezing point of 46 - 47°, inasmuch as it contains impurities. The chief impurities are 2,6- and 3,5-dinitrochlorobenzene, as well as the ortho-, para-, and to some degree, the meta-nitrochlorobenzenes, and 3,4-dinitro-1-chlorobenzene. The quantity of the latter depends upon the temperature conditions of the first stage of nitration. The higher the temperature of the first stage, the greater the yield of the undesirable 3,4-dinitro-1-chlorobenzene.

In addition to the impurities cited, dinitrochlorobenzene contains considerably

smaller quantities of dinitrobenzene and nitropolychlorides. These impurities

187 are formed in the nitration of benzene and the polychlorides contained in the initial chlorobenzene.

Dinitrochlorobenzene is virtually insoluble in cold water and is slightly soluble in hot water. 100 gms of water dissolve the following quantities of dinitrochlorobenzene, in gms:

at 15°	0,0008
at 50°	0,0410
at 100°	0,1590

Its solubility in 85% sulfuric acid (in %):

at 20°	about 1,7
at 50°	about 4,0
at 70°	about 6,5

This/solubility of dinitrochlorobenzene results in considerable losses thereof, degree of inasmuch as the spent acid contains 85% sulfuric acid. These losses may be eliminated by employing acid circulation, i.e., by utilizing the spent acid in the first-stage nitration.

Table 63 presents the solubility of dinitrochlorobenzene in organic solvents.

Table 63

a)	b)		
	15	30	50
Ethyl alcohol	8,2	18,8	—
Methyl alcohol	11,2	32,3	—
Ethyl ether	23,5	128,3	—
Chloroform	102,7	210,0	—
Ethyl acetate	119,4	—	297,5
Toluene	139,9	282,5	—
Benzene	153,1	339,5	—
Acetone	267,9	—	531,0

a) Solvent; b) Solubility, gms (per 100 gms of solvent) of dinitrochlorobenzene, at the following temperatures, °C

If a mixture of dinitrochlorobenzene and strong mixed acid is heated for 12 hrs at 130°, the result is picryl chloride, with a yield of 85% of theoretical (Bibl.204).

Dinitrochlorobenzene is readily saponified by bases, and forms dinitrophenolates. When it is saponified in the presence of alcohols, the consequence is ethers, such as dinitrophenetol, dinitroanisole etc.

In working with dinitrochlorobenzene, it must be borne in mind that its fumes are powerful irritants of the mucous membrane, and therefore the workshops must have good ventilation.

2,4-Dinitro-1-chlorobenzene is used to manufacture sulfur dyes. It condenses with a large number of compounds in the aromatic series, and the condensation products produced are reduced by sodium sulfide and sulfur.

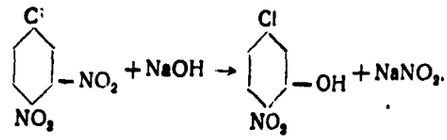
As already indicated, 2,4-dinitro-1-chlorobenzene is saponified by bases, to yield sodium dinitrophenolate:

$$C_6H_3(NO_2)_2Cl + 2NaOH \rightarrow C_6H_3(NO_2)_2ONa + NaCl + H_2O.$$

188 The reaction goes at high velocity even when weak alkali solutions are employed. The ease with which chlorine is substituted for by the hydroxyl is due to the presence in the molecule of dinitrochlorobenzene, of two nitro groups, in the ortho- and para-positions with respect to chlorine. The chlorine atom in chlorobenzene is saponified with difficulty by bases (the reaction will occur in an autoclave at a temperature of about 300°, and with strong caustic soda). Introduction of the nitro group into chlorobenzene activates the chlorine atoms. Even in the ortho- and para-nitrochlorobenzene, the chlorine atom is fairly easily exchanged for the hydroxyl, under the influence of a base. A nitro group in the meta-position with respect to the chlorine, does not activate it, and meta-nitrochlorobenzene usually does not saponify a caustic.

The saponification reaction of 2,4-dinitro-1-chlorobenzene is accompanied by the emission of heat, and this may induce a pronounced rise in temperature. To avoid processes of oxidation and possible flare-ups, the saponification of 2,4-dinitrochlorobenzene is performed at 100 - 105° by a weak aqueous alkaline solution (7%) used in very slight excess (1 - 2%) over the theoretically necessary.

Certain impurities in dinitrochlorobenzene - the ortho- and para-dinitrochlorobenzenes, are also saponified by caustic, and convert, correspondingly, to ortho- and para-nitrophenolates, which subsequently undergo transformation to picric acid. 3,4-Dinitrochlorobenzene reacts with caustic, but this is accompanied by an exchange not of the chlorine, but of the nitro group in the meta-position with respect to the chlorine, for hydroxyl, the consequence being 1-chloro-4-nitrobenzene, in accordance with the reaction:



Subsequently, upon nitration of dinitrophenol to trinitrophenol, this compound diminishes the quality of the latter.

As already indicated above, meta-nitrochlorobenzene does not saponify, but remains in the dinitrophenol as an impurity. Reduction in the quantity thereof may be achieved by increasing the period of time at which the reaction mixture is held at 105° toward the end of saponification, the meta-nitrochlorobenzene being driven off by steam under the circumstances.

Sodium dinitrophenolate is readily decomposed by dilute sulfuric acid, with liberation of dinitrophenol, in accordance with the reaction:

$$2C_6H_3(NO_2)_2ONa + H_2SO_4 \rightarrow 2C_6H_3(NO_2)_2OH + Na_2SO_4.$$

2,4-Dinitrophenol is a crystalline substance, bright yellow in color, having a freezing point of 112.5°, and a specific gravity of 1.683 (at 24°). The freezing point of 2,6-dinitrophenol is 62.5°. The 2,4-isomer crystallizes out of boiling water in the form of small platelets or in the form of pale yellow or, sometimes, completely colorless needles. When carefully heated at 70°, dinitrophenol undergoes slow volatilization. It can also be driven off with water vapor. Its solubility in 100 gms of water is, in grams:

at 8°	0,014
at 18°	0,507
at 100°	4,78

The solubility of dinitrophenol in organic solvents is illustrated in Table 64.

Dinitrophenol is acid in its properties and reacts with metals, oxides thereof, and carbonate salts, to yield dinitrophenolates, which are less sensitive than the corresponding picrates. With bromine, dinitrophenol forms dinitrobromophenol, melting point 119°.

189 Dinitrophenol is very toxic. It is essential that health and safety rules be adhered to when working with it.

Table 64

a)	b)	
	15	50
Pyridine	20,1	71,0
Acetone	35,9	98,3
Ethyl acetate	15,5	39,5
Benzene	6,4	25,7
Toluene	6,3	19,9
Chloroform	5,8	19,8
Methyl alcohol	4,9	16,9
Absolute ethyl alcohol	3,0	11,3
Ether	3,1	7,2
Carbon tetrachloride	0,4	1,8
Carbon disulfide	0,4	1,0

a) Solvents; b) Solubility (in 100 gms of solvent) of dinitrophenol, in gms, at the following temperature, °C

As an explosive, dinitrophenol is similar to dinitrobenzene. It is not employed by itself. During the First World War, an alloy of 40% dinitrophenol and 60% picric acid was employed in France.

c) Production of Trinitrophenol from Benzene by Oxidizing Nitration in the Presence of a Promoter

The production of trinitrophenol from benzene by nitration of the latter with weak nitric acid in the presence of mercury nitrate as promoter has been investigated by many scientists (Bibl.205, 206, 207). The most complete studies in the mechanization of this process, as well as its practical realization, are due to A.I.Titov and N.G.Laptev (Bibl.185).

Oxinitration (oxidation and nitration) of benzene to 2,4-dinitrophenol and to 2,4,6-trinitrophenol by mercury nitrate in nitric acid goes through the following stages:

$$C_6H_6 + Hg(NO_3)_2 \rightarrow C_6H_4HgNO_3 + HNO_3; \quad (1)$$

$$C_6H_5HgNO_3 + N_2O_4 \rightarrow C_6H_5NO + Hg(NO_3)_2; \quad (2)$$

$$C_6H_5NO + 2NO \rightarrow C_6H_5N_2^{\oplus} + NO_3^{\ominus}; \quad (3)$$

$$C_6H_5N_2^{\oplus} + H_2O \rightarrow C_6H_5OH + H^{\oplus} + N_2; \quad (4)$$

$$C_6H_5OH + HNO_3 \rightarrow \underset{(ortho)}{O_2NC_6H_4OH} + H_2O, \quad (5)$$

or

$$C_6H_5OH + HNO_3 \rightarrow \underset{(para)}{O_2NC_6H_4OH} + H_2O, \quad (6)$$

subsequent to which the mononitro derivatives are nitrated further.

A.I.Titov and N.G.Laptev regard reaction (3) and those which follow it (4) and (5) as not being the basic ones. According to their views, the basic

190 reactions subsequent to the decomposition of the mercury derivative and the formation of nitrophenol are the following:

$$C_6H_5NO + 3HNO_3 \rightarrow C_6H_3(NO_2)_2OH + 2HNO_2 + H_2O;$$
$$C_6H_3(NO_2)_2OH + HNO_3 \rightarrow C_6H_2(NO_2)_3OH + H_2O;$$
$$HNO_2 + HNO_3 \rightarrow N_2O_4 + H_2O.$$

According to the mechanism envisaged by A.I.Titov and N.G.Laptev, the total

expenditure of nitric acid in the formation of one mole of trinitrophenol is 5 moles, and one mole of the dimer nitrogen dioxide, is formed simultaneously.

Production of trinitrophenol by this mechanism is carried out by circulation of benzene through 50% nitric acid, containing 3.5% mercury nitrate. The reaction occurs at 50°. The benzene, saturated with nitro derivatives, and having a specific gravity of not less than 1.2, is removed from the cycle. The spent benzene is heated at 60° for 24 hrs, and the dinitrophenol is nitrated by the nitrogen oxides in the benzene to picric acid. Upon completion of the reaction, the mixture is cooled to 5 - 7°, and the crystallized picric acid is filtered off the benzene, which is returned to the cycle.

A necessary condition for introducing oxidizing nitration into production is regeneration of the mercury. Only if this problem is satisfactorily solved can oxidizing nitration successfully compete with other methods (Bibl.208).

Section 2. Properties and Applications of Trinitrophenol

Picric acid or 2,4,6-trinitrophenol is a crystalline substance existing in two polymorphic forms. The crystals obtained from the alcohol solution are orthorhombic in shape, bright yellow in color, having a freezing point of 121.3° and a melting point of 122.5° (Bibl.183). The specific gravity of crystalline picric acid is 1.763, and that of the liquid acid is 1.589 (at 124°).

The gravimetric density if 0.9 - 1.0, and the density of the cast picric acid is 1.61 - 1.67. Pressing at a pressure of 2000 kg/cm^2 yields a density of 1.63. By increasing the pressure to 4125 kg/cm^2, it becomes possible to increase density to 1.74. The latent heat of fusion of picric acid is 20.4 kcal/kg, and the specific thermal capacity of 0.234 cal/gm. Picric acid is virtually non-hygroscopic. When

[illegible] fused, it volatilizes to a limited degree: vapor pressure 195° - 2 mm Hg, and at 225° - 50 mm Hg (Bibl.183).

Tables 65 - 67 illustrate the solubility of picric acid in water and other solvents.

Table 65

a)	b)	a)	b)
0	1,05	40	1,98
5	1,07	50	2,53
10	1,10	60	3,17
15	1,16	70	3,89
20	1,22	80	4,66
25	1,37	90	5,49
30	1,55	100	6,33

a) Temperature, °C; b) Solubility, g of picric acid in 100 gms water, gm

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Table 66

a)	b)		
	18	50	80
0	1,184	2,389	4,541
2,3	0,0230	0,692	1,940
4,7	0,142	0,368	1,251
10,0	0,091	0,265	0,727
18,0	0,049	0,214	0,561
25,5	0,092	0,230	0,587
50,5	0,429	0,645	1,104
69,7	0,928	1,424	2,203
87,9	2,461	5,826	7,610
97,4	7,532	12,785	24,024
100,0	10,180	16,230	25,860

a) Strength of sulfuric acid, %; b) Solubility, gm, of picric acid (in 100 gms acid), at temperature, °C

Table 67

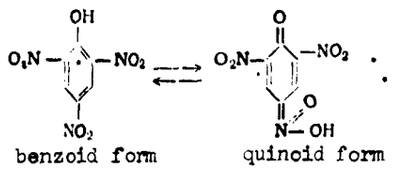
a)	b)											
	15	20	27	35	38	42	48	51	56	60	65	78
c)	—	5,9	—	—	—	—	—	—	—	—	—	40
d)	—	3,45	—	—	—	—	—	—	—	8,4	—	—
e)	—	28,3	—	33,3	—	38,3	—	42,5	46,2	—	—	—
f)	9,1	—	12,3	14,3	16,7	—	22,7	—	29,4	—	39,7	—
g)	6,8	8,8	11,4	17,6	—	23,5	—	—	33,5	—	41,7	50

a) Solvent; b) Solubility of picric acid, %, at temperatures in °C; c) Alcohol; d) Dichlorobenzene; e) Nitrobenzene; f) Dichloroethane; g) Benzene

Picric acid dissolved in ether, methyl alcohol, glycerin, chloroform, carbon disulfide, and also in resins and lacquers. The solubility of picric acid in water and in sulfuric acid is of practical interest. In view of its considerable solubility in water, hot water cannot be employed to wash picric acid.

Aqueous solutions of picric acid are yellow in color, while solutions of picric acid in sulfuric acid and ligroin are colorless. A similar phenomenon occurs in the cultivation of crystals of picric acid. Ordinary industrial picric acid is yellow, but picric acid recrystallized from sulfuric or hydrochloric acid is virtually colorless.

Certain hypotheses exist with respect to the reason for the coloration of picric acid. It is held that undissociated picric acid is colorless, but that the $[C_6H_2(NO_2)_3O]^{\ominus}$ ions are yellow. Other views hold that the coloration of nitrophenols, including picric acid, depends upon the fact that they exist in two tautomeric forms: the benzoid and the quinoid:



benzoid form quinoid form

192 Both these forms are in equilibrium, and the equilibrium is shifted in the direction of formation of the quinoid form. The quinoid form of picric acid is colored, and the benzoid is colorless. In the opinion of Hantsch, as already indicated, salts of the nitrophenols have the quinoid form.

Picric acid and its solutions color tissues of animal origin (wool, silk, hair, skin) yellow. As is the case with other nitro compounds, they form complexes that crystallize well (Bibl.209); for example, with naphthalene, they form golden yellow crystals having the following composition $C_{10}H_8\ C_6H_2(NO_2)_3OH$. This reaction is frequently employed to separate picric acid.

A characteristic reaction for picric acid is provided by KCN, which forms isopurpuric acid with it. This is a red compound (qualitative determination of small quantities of picric acid).

Upon reduction, picric acid converts to triaminophenol. This reaction is employed to get rid of the picric acid in wash waters as otherwise they dirty and poison bodies of water.

Nitric acid dissolves picric acid, and virtually does not react with it (Bibl.210). Bleaching lime converts picric acid, in the presence of water, to chloropicrin $CCl_3(NO_2)$ (a poison).

Picric acid is a somewhat stronger acid than carbonic acid. It reacts with carbonates to liberate CO_2 and form picrates. In the presence of moisture, picric acid decomposes cellulose and glycerol nitrates, as well as ammonium nitrates, cleaving HNO_3 away therefrom. Therefore, it can be used in a mixture with these components. In the presence of moisture, picric acid reacts with virtually all metals (other than tin and the noble metals), yielding salts

(picric). Picric acid reacts with metal oxides or carbonates salts more readily than with metals (Bibl.211).

The majority of picrates are more soluble in water than is picric acid, but, nonetheless, they are not soluble in dry benzene. This property is employed to determine picrates in picric acid.

All picrates are solid crystalline substances having substantially greater sensitivity to water and friction than does picric acid. The greatest sensitivity is that of lead and iron picrates. In sensitivity, lead picrate is similar to lead azide. Minimum sensitivity is displayed by the picrates of sodium and ammonium. The latter is employed to fill shells. The shock sensitivity of picrates is illustrated in Table 68.

Table 68

a)	b)	c)	a)	b)	c)
Picric acid	95	300	Iron picrate	7	300
Sodium picrate	80	360	Lead picrate	5	260
Zinc picrate	60	315	Silver picrate	5	—
Copper picrate	7	310	Lead azide	4	—
			Mercury fulminate	2	210

a) Explosive; b) Height from which weight is dropped (2 kg), cm; c) Detonation point, °C

In the process of production of picric acid, picrates may come into being in the washing and drying process, as a consequence of the presence of salts in the wash water. Salts reacting with picric acid yield picrates, which remain in the picric acid in greater quantity, the more poorly the separation was performed. Therefore, the washing of picric acid should be performed with soft water (not containing salt), and before it is sent to drying, the product should be thoroughly centrifuged from the wash water on a hard-rubber or

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tin-plated centrifuge. To avoid the formation of picrates as washed picric acid contacts metal, the washing and drying portions of the apparatus should preferably not be of metal, or, in any case should consist of certain particular metals (aluminum, tin-plated copper, bronze).

The possibility that picrates may be formed by direct reaction between picric acids and metals in the process of nitration is eliminated by the presence of sulfuric acid in the nitro mixture. The formation of picrates may occur upon reaction of picric acid with alkali earth bases and salts in cement floors, and therefore cement must not be used for flooring in picric acid production.

When the aqueous solution of picric acid is saturated with ammonia, ammonium picrate results.

Ammonium picrate is a crystalline substance (yellow or red in color, in different modifications), having a specific gravity of 1.72, fusing at 265 - 270° (Bibl.183), and having a detonation point of 290°. Ammonium picrate dissolves readily in boiling water (74.8 gm per 100 gm water at 100°) and less satisfactorily in cold water (1.1 gm per 100 gm water at 20°). It is considerably more hygroscopic than picric acid, and when stored in a moist atmosphere for a month, absorbs more than 5% water. It is insoluble in benzene. Completely dry ammonium picrate undergoes virtually no reaction with metals and their oxides, whereas moist picrate reacts, but more slowly than does picric acid.

Ammonium picrate is a comparatively unstable substance, and when heated to 220°, vigorous decomposition, with liberation of ammonia, sets in:

$$C_6H_2(NO_2)_3ONH_4 = C_6H_2(NO_2)_3OH + NH_3.$$

This reaction also proceeds at a lower temperature. If ammonia be removed from the reaction sphere, considerable decomposition of ammonium picrate is possible

(and consequently, accumulation of picric acid when it is stored for a long period in conditions other than airtight).

In the United States, ammonium picrate is produced on the industrial scale in the following way: when heated, one part picric acid per weight is dissolved in 10 - 12 parts water per weight, to which 20% ammonium picrate is added until complete neutralization is achieved (0.4 - 0.5 parts per weight), and upon cooling, ammonium picrate comes down, which is filtered, washed, and dried.

Ammonium picrate does not react with salts, inasmuch as the hydrogen of the hydroxyl group therein has already been replaced by the NH_4 group. Previously, ammonite of the following composition: 72% NH_4NO_3 and 28% picrate ("gromoboy" or "maisite") was manufactured on ammonium picrate as base.

Ammonium picrate is less shock-sensitive than picric acid. It detonates when a weight of 2 kg is dropped from a height of 100 cm. The heat of explosive decomposition is 800 kcal/kg, and the rate of detonation (at Δ = 1.63) is 7150 m/sec (Bibl.183).

In the United States, demolition shells armor-piercing and used to be filled with ammonium picrate (by the method of pressing).

Picric acid also forms picrates with organic bases. Thus, for quantitative determination of picric acid, employment is made of acridine picrate $C_{13}H_9N \cdot C_6H_2(NO_2)_3OH$ which is poorly soluble in water, benzene, and alcohol.

Quantitative determination of picric acid may be formed with the aid of nitron, with which picric acid yields a picrate poorly soluble in water.

194 Picric acid is poisonous, and therefore the appropriate safety rules have to be adhered to in working with it.

In the pure form, picric acid is very stable to the usual temperatures of storage. A small quantity thereof may even be subjected to volatilization by heating to 125 - 130°. At 160°, one observes slight decomposition of picric acid with liberation of gases, and deflagration occurs at 300 - 310°. Ignited picric acid burns slowly, with a smoky flame, in the open air or in wooden packaging.

When hot used picric acid is brought into contact with iron, slaked lime, or salt solution, and the like, the entire mixture explodes, as a consequence, apparently, of the formation of highly-sensitive picrates. To avoid this, the walls of storehouses and factory buildings housing this material must be covered with a gypsum plaster, and electrical equipment must not include either lead or iron, but only aluminum or copper, as these metals form compounds with picric acid only with difficulty.

Upon rapid heating in an enclosed shell, to 300°, picric acid explodes. Picric acid is more sensitive than TNT to shock. It explodes when a 2 kg weight is dropped from 80 cm, whereas TNT requires dropping from 100 cm.

Because of the comparatively high shock sensitivity of picric acid, the pure product is employed only to fill small and medium-caliber shells. Large-caliber shells are filled with mixtures of picric acid and dinitronaphthalene.

Addition of silica considerably increases the sensitivity of picric acid to shock, as is evident from Table 69.

Table 69

a)	b)	c)
0	25	25
0,25	25	60
0,50	25	100

a) Percent silica sand in picric acid; b) Number of tests (10 kg [illegible] 25 cm height); c) Complete explosions, %

In the pressed or cast form, picric acid is less shock-sensitive than in the powder form.

When pulverized picric acid is subjected to friction between plates of hard metals (iron, steel) and stones it explodes.

The explosive properties of picric acid are as follows: volume of gases 730 ltr/kg, heat of explosion 1050 kcal/kg, temperature of explosion 3300 - 3500°, expansion in Trauzl block 305 cc, Hess brisance 16 mm, rate of detonation 7350 m/sec.

Picric acid is employed both in the pure form and in mixtures with nitro compounds to fill munitions. The addition of nitro compounds reduces the sensitivity of picric acid to mechanical influences and permits the filling of large-caliber shells with alloys thereof.

The most widely employed picric acid alloys were: the French mixture (80% picric acid and 20% dinitronaphthalene) having a melting point of 104°, and the Russian mixture (51.5% picric acid and 48.5% dinitronaphthalene) having a melting point of 82 - 87°, and also an alloy consisting of 60% picric acid and 40% dinitrophenol (melting point 85°), and an alloy consisting of 60% trinitrocresol

and 40% picric acid (melting point 85°). The use of readily fusible alloys makes it possible to fill shells with molten explosives without having to heat them excessively.

During World War II, picric acid was employed in Germany to fill hand grenades, detonators, aircraft bombs (in the form of a mixture with dinitronaphthalene) and certain special shells (explosive smoke shells).

When picric acid is employed to fill shells, special attention must be given to providing complete isolation thereof from the shell casing and the detonator. This was previously done by covering the interior of the shell with tin plate or lacquer. This method does not provide a complete guarantee of isolation of the picric acid, because of the difficulty of monitoring the quality of the covering. A more reliable method is the cartridge-type of filling. The explosive charge of picric acid is placed in a paperboard or some other nonmetallic container and is thus kept divided from the shell casing. Assembly of the two into a unit is performed not too long a time prior to the employment of the shell. The Japanese used this method as far back as the Russo-Japanese War.

Section 3. Technology of Trinitrophenol Production

a) Production of Picric Acid from Phenol

The method of obtaining picric acid from phenol was developed and widely employed on an industrial scale as far back as the last century. Subsequently, this method underwent considerable technological changes. The major improvement was employment, for sulfurization and subsequent nitration, of phenol instead of weak acids (92% sulfuric and 45% nitric acid), strong

acids (oleum and melange). The use of strong acids made it possible to employ cast iron instead of ceramics for the apparatus. The use of metal in making the apparatus, in turn, made it possible to make them of more advanced design. Apparatus came to be produced with mechanical agitators, as well as with jackets and coils for the delivery of coolant water therein. This facilitated the attainment and sustaining of precise conditions of temperature.

The production of picric acid consists of the following operations: 1) sulfonation of the phenols; 2) nitration of the phenol sulfonic acid; 3) separation of the product from the acid and washing with water; 4) drying of the washed picric acid; 5) separating into batches and packaging of the finished product. Moreover, there are usually special workshops to purify the wash water and the spent acids.

The production of picric acid from phenol in batch-type apparatus is diagramed in Fig.60.

The phenol is carried, in zinc-plated drums, on cars (1) and is raised to the top of the building by means of an elevator (2). The drum is placed in a melting device (3), provided with a jacket into which steam is emitted. As fusion of the phenol occurs, it flows through a hole in the bottom of the drum and through the bottom flange of the melting device into a metering tank (4), which stands on scales. The metering device is provided with a coil for delivery of steam so as to keep the phenol in molten condition.

Sulfonation is performed in a sulfurator (5), which is a cylindrical cast-iron vessel with a spherical bottom and cover, and provided with a steam jacket. The sulfurator contains a coil for water, and an impeller agitator for stirring. A

specific quantity of oleum (computed in terms of H-sulfonation) is charged via the measuring tank (6), and the phenol is added slowly, over the course of an hour, with the agitator in operation. The phenol is run in under conditions of a gradual increase in temperature from 20 to 90°. Upon completion of the
196 run-in, the mixture is held at 100° for 3 hrs, then is sent to the collector (7), and then to the metering tank (8), for delivery to the nitrator (11).

Monitoring of the sulfonation process is performed by observation of the sulfonation temperature and analysis of the sulfo mixture for acidity, which, after holding, should not be less than 64% in terms of H_2SO_4.

The process of nitration is performed in apparatus of the same design as sulfurator. The nitrator is made of cast iron. The solution of disulfophenol is charged into nitrator (11), and spent acid (2.13 parts by weight per part phenol by weight) is run in from metering tank (10), for dilution, inasmuch as formation of the picric acid yields a mass so thick as to render difficult the escape of the nitrogen oxides, with the consequence that the mass foams. Nitration is by melange, which is run in from metering tank (9). The amount of melange is calculated to deliver 3.75 gm-moles HNO_3 per 1 gm-mole phenol. The total melange is divided into three parts, in a ratio of 4:4:5, run in at various temperatures. The first part begins to be run in at 40°, and run-in terminates at 60°; run-in of the second part is terminated at 80°, and of the third part at 100°. During the third stage of nitration, after approximately 2/3 of the melange has been run in, crystals of picric acid starts to come down. Run-in continues for about 3 hrs.

Upon completion of run-in, the mixture is held for 1 hr at 100°, whereupon the contents of the apparatus are cooled to 30°, and are transferred through collector (12) to funnel (13), which serves to supply the centrifuges. Settling out of the acid from the product and of the mechanical impurities from the acid is performed therein over a period of 10 - 12 hrs. As settling occurs, the picric acid floats to the top, while the spent acid accumulates at the bottom of the funnel, and the mechanical impurities (mineral salts and others) settle at the bottom of the funnel. After settling, a portion (60 - 65%) of the spent acid is let out of the funnel into collector (21). All the mechanical impurities that have settled out are dumped along with the acid.

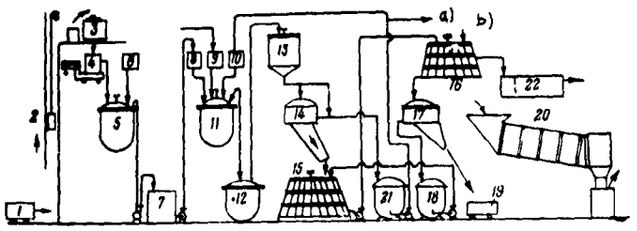


Fig.60 - Diagram of Production of Picric Acid from Phenol

1 and 19 - Cars; 2 - Elevator; 3 - Melting device; 4, 6, 8, 9, and 10 - Measuring tanks; 5 - Sulfurators; 7, 12, 18 and 21 - Collectors; 11 - Nitrator; 13 - Settling funnel; 14 and 17 - Centrifuges; 15 and 16 - Decanters; 20 - Drying drum; 22 - Trap

a) Acid to recovery; b) Water

After the discharge of a portion of the spent acid from the funnel, the stirrer is started, and the remaining turbid mass of spent acid, along with the picric acid, is discharged to [illegible] centrifuge (14), where the spent acid is centrifuged away from the product. The centrifuged acid goes to collector (21),

unloaded
and the picric acid is [illegible] into decanter (15) (a wooden tank), into which acid wash water had previously been run from collector (18), this being the water from the washing in the previous operation.

The contents of decanter (15) are stirred with a mechanical wooden agitator, and the acidity of the water rises to 3 - 3.5% due to the spent acid remaining in the picric acid. The picric acid, which is turbid in the acid water, is pumped to the [illegible] upper decanter (16) where it is permitted to settle for
197 10 - 15 min, and the wash water, having an acidity of 3 - 3.5% (minimum solubility of picric acid) and being [illegible] in a quantity of 3 parts by weight to one part by weight of product, is discharged through the upper drainage flange to trap (22), from which it goes to purification. After discharge of the acid water, pure water is run into decanter (16) (2 parts by weight per 1 part product by weight), the mass is mixed, and discharged to [illegible] centrifuge (17), where the water is separated from the [illegible] picric acid, and [illegible] it is washed once again with cold water (1 part water by weight to 1 part product by weight). The wash water is collected in collector (18), and is used for first washing.

Thus, water circulation is employed in the washing of picric acid. The consumption of water is 3 tons per 1 ton of picric acid, with the consequence that there is a considerable [illegible] reduction in picric acid losses in washing.

At some plants, the washing of [illegible] picric acid is performed in a somewhat difference fashion.

The acid product is charged into a decanter, into which acid water from the preceding second washing of product and final washing on the centrifuge has previously been run in. The product is mixed in the decanter, then permitted to

settle, and the acid water is discharged through the upper flange. Fresh water is then added, heated to 90°, and the entire mass is stirred at this temperature for 1 hr, whereupon it is cooled, and the product is permitted to settle out of the acid water. After the second washing, the acid water is run into a receiver, and the product is discharged into a centrifuge. On the centrifuge, the product is separated from the acid water, and washed with fresh water. The wash water goes from the centrifuge to the receiver, and is mixed with water from the second washing of the picric acid. This water is then employed for the first washing.

Thus, the washing is performed in a single decanter, also with return water.

The second method of washing picric acid permits a reduction in the acidity of the product (to less than 0.1%), thanks to the use of hot water, and simultaneously improves its quality. This method of washing was employed chiefly in the production of picric acid from benzene, through the dinitrochlorobenzene intermediate.

The spent acid, having settled out in collector (21), is employed in part to dilute sulfophenol, whereas the rest goes to recovery and further to denitration. The product, having undergone a final centrifuging on centrifuge (17), is discharged into car (19) and transported to the drying division.

Picric acid, after washing, should be of not more than 0.1% acidity, or more than 10% moisture content. It is dried in drum drier (20).

In designing driers for the drying of picric acid, it is necessary to bear in mind that this acid reacts with metals and forms picrates. Therefore, wood or aluminum, which do not react to picric acid, are the preferable materials for the desiccators.

Ceilings in these buildings are made of wood, and roofs are covered with tar paper. Concrete must not be used, inasmuch as picric acid, being stronger than silicic acid, displaces SiO_2 in the concrete from its compounds of metals, to form picrates (Ca, Mg, Fe, Na, and others) which may be cause[illegible] for accidents. A strong shock or friction causes the picrates to flash, and this may result in a fire or explosion. Floors should also preferably be made of wood, covered with [illegible] linoleum, which facilitates washing of the floor and protects the wood against permeation by picric acid.

The dried picric acid is hauled in boxes on cars to the packaging department, where it is sieved through copper mesh and packaged in wooden boxes or containers
198 lined with paper. The yield of picric acid is 85% of theoretical. Picric acid has to satisfy the technical specifications indicated in Table 70.

Table 70

[illegible]	[illegible]	[illegible]	[illegible]
Appearance (all grades)	Crystalline powder, without [illegible] mechanical impurities		
Color	Bright yellow		
Freezing point, °C, less than	119,5	119,5	119
Benzene-insoluble residue, %, not more than	0,2	0,3	1,0
H_2SO_4 content, %, not more than	0,1	0,2	0,3

a) ~~Properties;~~ b) ~~Grade~~ 1; c) ~~Grade 2;~~ d) ~~Grade~~ 3

The quality of the picric acid is determined by the [illegible] purity of the initial phenol.(absence of cresols [illegible] therefrom), and also by the lack of incompletely nitrated dinitrophenol. The quantity of impurities insoluble in benzene may be increased by the dinitrophenol sulfonic acid (not converted into picric acid) which undergoes partial dissolving in the picric acid.

. Spent acid, of the following percentage composition, is a picric acid byproduct:

H_2SO_4	77 - 79
HNO_3	0.1 - 1
N_2O_3	4 - 5
Oxalic acid	1 - 1.5
Dinitrosulfophenol	0.5 - 1.5
Picric acid	1.5 - 2
Water	residue

This spent acid must not be sent directly to denitration, as, upon denitration and concentration, the picric acid will be ~~xxxxxx~~ volatilized and will deposit upon the apparatus and piping, which may be a cause of accident. As a consequence, the spent acid is subjected to special cleaning, before denitration, with the object of extracting the nitro products. Usually, they are extracted by organic solvents.

A second ~~xxxxxx~~ waste product of picric acid production is the wash water, which contains as much as 1.8% picric acid in solution and suspension. This water is of substantial toxicity, and therefore it must undergo purification before being dumped into bodies of water (Bibl.212).

In industry, the spent water is purified by reduction of picric acid to triaminophenol by iron filings. 5.4 gm iron filings are consumed in the reduction per 1 ltr of wash water containing 0.4% picric acid. At a temperature of 15 - 20° the process is completed in 8 - 10 min. The triaminophenol obtained as a result of reduction is then oxidized by atmospheric oxygen, with destruction of the benzene ring. To perform reduction by iron filings, the acidity of the wash water must be

no less than 7 - 8%, i.e., the water going to purification must be acidified. It is usually acidified with spent acid. The purification process is illustrated in Fig.61.

The wash water is delivered to receiver (2) and acidified with spent acid from the pressure tank (1). Agitation during acidification is by means of compressed air. Usually two such tanks are provided, which work alternately. The
199 acidified wash water is delivered from them by pump, continually, through metering device (3), to apparatus (4) for reduction.

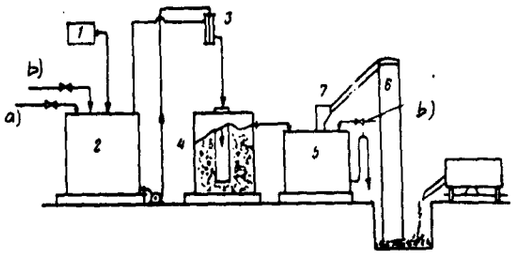


Fig.61 - Diagram of Purification of Spent Water

1 - Pressure tank; 2 - Receiver; 3 - Metering device; 4 - Apparatus for reduction; 5 - Neutralizer; 6 - Elevator; 7 - Hopper

a) Wash water; b) Compressed air

The reduction apparatus is an ordinary cylindrical wooden tank containing a wooden pipe that does not reach to the bottom. The tank is filled with iron filings. The water enters the upper portion of the pipe, passing through it to the bottom of the apparatus, and rises through the iron filings, going out of the upper portion of the apparatus.

From the reducer, the acid water goes to a wooden neutralizer (5), where it is neutralized with lime. The lime is delivered continually, in controlled quantity,

by elevator (6) through hopper (7). Agitation in the neutralizer is performed by compressed air. The purified water goes from the neutralizer through a system of traps into the sewerage system.# The process of purification is run at normal temperature.

b) Production of Picric Acid from Benzene through Dinitrochlorobenzene as Intermediate

The production of picric acid through dinitrochlorobenzene as intermediate should be organized at plants that manufacture chlorine and are near benzene plants. This makes it possible to chlorinate the benzene with gaseous chlorine, without necessitating large expenditures to compress chlorine and transport it in cylinders. The production is performed in four major departments: the chlorobenzene, the dinitrophenol, the picric acid and the picric-acid drying.

Chlorobenzene department. Figure 62 illustrates the production of chlorobenzene (Bibl.213, 214).

Benzene from tank (1), and gaseous chlorine, are delivered to the lower portion of the chlorinator (2). The chlorinator is a steel column with acid-resistant lining, having a packing of steel and ceramic rings. The upper (wider) part of the chlorinator serves as a spray-catcher, and the hydrogen chloride formed in chlorination is removed from its very top, along with benzene and chlorobenzene fumes. The amount of benzene vaporized is 1.4 - 1.5 ton per 1 ton of chlorobenzene obtained.

The gases emitted from the chlorinator are sent to a reflux condenser (3) with graphite tubes impregnated with phenol-formaldehyde resin. Here the gases and fumes are cooled to 30°, and about 90% of the benzene contained

in the vapors condenses. The benzene is separated in separator [illegible] (4), and the remaining fumes and gas go to a mixing condenser (5), where they are cooled

200 to -2°. More than 9% additional benzene is separated thereby.

The mixing condenser is a packed column through which the chlorobenzene flows. The benzene fumes condense, and the solution of benzene and chlorobenzene flows out of the bottom of the [illegible] apparatus. A portion of the solution is again directed to flow through the mixing condenser via condenser (7). Benzene is separated from the other portion of the solution in fractional distillation column (8). In order to prevent the chlorobenzene from becoming saturated with the condensing benzene, which may result in solidification of the solution upon cooling, fresh chlorobenzene is added to the circulating solution in collector (6).

From the chlorinator (2), the reaction mixture goes with the solution taken off condenser (5), to separation in a two-column fractionating unit, employing a continuous process. The mixture, entering fractionating column (8), contains 64 - 65% benzene, 33.5 - 34% chlorobenzene, about 1.5% polychlorides, and a small amount of dissolved hydrogen chloride and ferric chloride. At some plants, the reaction mass is treated with a weak solution of caustic alkali before fractionation, to neutralize the HCl and decompose the $FeCl_3$.

The temperature in the vat part of column (8) is maintained within the limits of 133 - 141°, and in the upper portion, within 75 - 88°. The distillate driven off the column contains 99.5% benzene and 0.5% chlorobenzene. Raw chlorobenzene, containing 0.15 - 0.25% benzene and 3.5 - 4.5% polychlorides flows directly from the vat portion of the column. Commercial chlorobenzene is driven off the raw material in column (12). The resultant chlorobenzene contains 0.3 - 1.1%

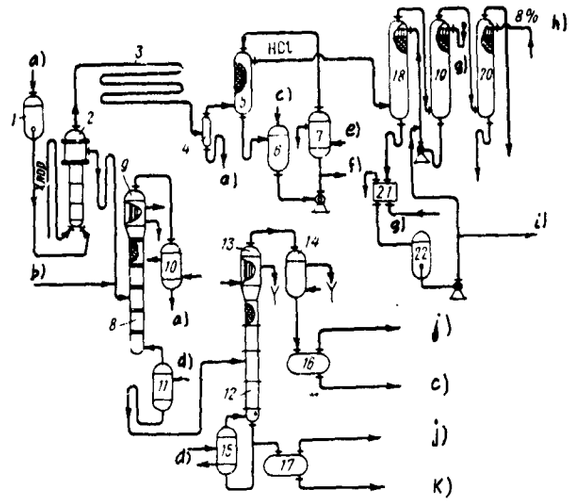


Fig.62 - Diagram Showing Continuous Chlorination of Benzene

1 - Pressure tank; 2 - Chlorinator; 3 - Trickle condenser; 4 - Separator; 5 - Mixing condenser; 6 - Intermediate collector; 7 - Condenser; 8 and 12 - Fractional distillation; 9 and 13 - Fractionating column; 14 - Condensers; 11 and 15 - Boilers; 16 and 17 - Vacuum collectors; 18 and 19 - Absorbers; 20 - Neutralizing column; 21 - Graphite condenser; 22 - Sulfuric acid collector

a) Benzene; b) From apparatus (5); c) Chlorobenzene; d) Steam; e) Lime; f) To apparatus (8); g) Water; h) 8% caustic solution; i) Hydrochloric acid; j) To vacuum pump; k) Polychlorides

polychlorides and about 0.3% benzene. The chlorobenzene content of the mixture of polychlorides flowing out of the column vat usually does not exceed 10%. This mixture may be employed to produce tetra- and hexachlorobenzene.

201 Hydrochloric acid is obtained from the hydrogen chloride formed on chlorination. To do this, the hydrogen chloride discharged from the mixing condenser (5) goes to three column-type apparatus connected in series (18), (19), and (20), of which the first two (in the direction of gas flow) (18) and (19) serve as absorbers, whereas neutralization

of the residual hydrogen chloride occurs in apparatus (20). Absorber (18) is irrigated with dilute hydrochloric acid. The strong hydrochloric acid emerging from it is cooled to 20 - 30° in the graphite condenser (21). A portion of the strong hydrochloric acid is returned to absorber (18) to increase the density of irrigation.

The gases emitted from absorber (18) are sent to the second absorber (19) for absorption of the residual hydrogen chloride. The resultant dilute hydrochloric acid goes to irrigate absorber (18). To neutralize the residual hydrogen chloride, the gas is sent to column (20), irrigated by an 8% aqueous solution of caustic.

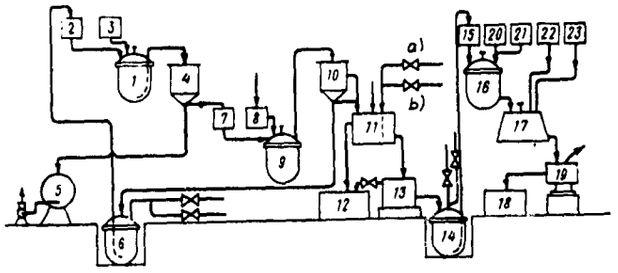


Fig.63 - Diagram of Production of Dinitrophenol from Benzene

1 - Extractor; 2,3,7,8,15,20,21,22,23 - Metering tanks; 4,10, and 13 - Separators; 5 - Receiver; 6 and 14 - Rising devices; 9 - Nitrator; 11 - Washing vat; 12 and 18 - Traps; 16 - Saponifier; 17 - Apparatus for decomposition of sodium dinitrophenolate; 19 - Centrifuge

a) Steam; b) Compressed air

Dinitrophenol shop. The production of dinitrophenol from chlorobenzene may be performed in accordance with the mechanism illustrated in Fig.63.

In extractor (1), which is an iron vat enclosed in a jacket, spent acid is charged in from metering tank (2), and cooled to 45°. Then, chlorobenzene (1 part

per 2.5 parts spent acid) is gradually added from measuring tank (3). During the charging period, the temperature is adjusted so as not to rise above 55 - 60°. After run-in and mixing to follow it, the extractor contents are transferred to separator (4) over a 20 min period. The purpose of the operation is the chlorobenzene extraction from the spent acid of the dinitrochlorobenzene dissolved therein (about 2 - 5%). and utilization of the residual HNO_3 (1.5 - 2%).

The spent acid remaining in the separator is sent to receiver (5), and from there to denitration, and the utilized ("stirred") chlorobenzene is sent to measuring tank (7) for nitration. Nitration of the chlorobenzene to dinitrochlorobenzene is performed in a single stage. To accomplish this, a nitro mixture consisting of 65 - 66% H_2SO_4, 28 - 29% HNO_3, and 5 - 6% H_2O. is poured into nitrator (9) from measuring tank (8).

The amount of mixture is determined on the basis of 10% excess HNO_3 over the theoretical. The chlorobenzene is added to the nitro mixture over a 3-hr period, with temperature rising slowly from 20 to 45°. Upon completion of the run-in, the nitro mass is heated for an hour to 105 - 110°, and then held at that temperature another 30 min. At the end of the operation, the dinitrochlorobenzene must be solidified at a temperature not below 47°.

202 Upon completion of nitration, the contents of the apparatus are forced into separator (10) by compressed air (this is a cylindrical vessel with a conical base), and are permitted to stand for 3 hrs. The dinitrochlorobenzene that settles out of the spent acid is drained, by means of a valve with a connecting piece to the washing vat (11) and the spent acid goes to the rising device (6) from which it

is delivered for [illegible] extraction.

The washing vat (11) has a bubbler , with steam and compressed air attached. Water is run into the vat, which is then heated by live steam to 70°, whereupon the dinitrochlorobenzene is run in (1.5 part water per part dinitrochlorobenzene). After agitation by compressed air, and settling, the wash water is drained and fresh water is run into the vat. Four such washings are made, [illegible] followed by a fifth with soda (3% solution), and then another one or two water washings (until the residual acidity of the product is 0.02%).

The wash waters go to trap (12) and the dinitrochlorobenzene to separator (13), for the fullest possible separation from the water. The separator (13) has a coil for heating. Settling is performed at a temperature of 70 - 80°. After settling for an hour to free it from water, the product is sent to [illegible] saponification by rising device (14). The saponifier (16) is an iron pot with jacket or coil for heating, and an impeller agitator. Water heated to 75°, and a 25 - 30% caustic solution are run into the saponifier from metering tanks (20) and (21). Caustic soda is in 85% [illegible] excess over the theoretical, and the [illegible] water is calculated to yield a 7.5% NaOH solution for saponification.

Because of the exothermic reaction involved in saponification, the temperature rises to 93 - 95° during the run-in of dinitrochlorobenzene from [illegible] metering tank (15). The mixture is then heated to 100° and held there until saponification is completed (20 - 30 min).

The completion of saponification is monitored by a sampling for the absence of dinitrochlorobenzene, which is performed as follows: [illegible] 5 cc phenolate is dissolved

in 20 cc hot water, and acidified with 10% sulfuric acid until acid reaction is observed. If drops of oil appear at the bottom of the test tube, this will testify to the presence of dinitrochlorobenzene. The absence of drops of oil indicates that saponification has been concluded. A second control is titration with free caustic, the strength of which should be 0.4 - 0.8%.

In order to decompose the sodium dinitrophenolate, the mixture, at temperature 100°, is discharged from the saponifier into apparatus (17), consisting of a wooden vat with coil, lead bubbler , and agitator. Water and spent acid from picric acid production is run into the apparatus beforehand from measuring tanks (22) and (23). In order to bring about decomposition, spent acid, in 8% excess over the theoretical, and water calculated to yield a 10% sulfuric acid solution, are employed. Sodium dinitrophenolate solution, from the saponifier, is charged into the sulfuric acid solution over a 25 min period, with stirring. After this run-in, the mixture is held for 20 min at 75°. The operation is monitored by determining the acidity of water in the bath, which should not be less than 0.3%.

When the holding period is completed, the apparatus contents are cooled by water (via a coil) to 35°. Further cooling to 25 - 30° is performed by addition of cold water to the apparatus.

Upon conclusion of the operation, the mixture in the apparatus is drained to centrifuge (19), running at low speed, where it is washed with water, after which the centrifuge is switched to high speed for better removal of the water. The centrifuged water goes to trap (18). The dinitrophenol, having a moisture content of 10 - 13% goes to picric acid production.

Picric acid is produced by nitration of dinitrophenol in an ordinary batch-type

iron nitrator (Bibl.215). Spent acid and 20% oleum is charged into the nitrator in quantities calculated to yield a 94 - 95% sulfuric acid (2.5 parts

203 medium per part dinitrophenol by weight), whereupon the moist dinitrophenol is run-in. The apparatus contents are heated to 30°, whereupon, over a period of 3 - 3.5 hrs the nitrating mixture is run in, and the temperature at the end of the period of run-in is raised to 55°. The acid nitrating mixture has the following composition: 71 - 72% H_2SO_4 and 28 - 29% HNO_3. It is run in to yield a 50% excess of nitric acid over the theoretical. After the mixed acid has been run-in, the reaction mixture is slowly heated for 1 - 1.5 hrs to 110 - 112°, and held at that temperature for 1.5 hrs. It is then cooled to 30° over a period of 2.5 hrs, and removed by compressed air to the settling funnel. After settling, a portion of the spent acid is discharged into a receiver, and the remaining spent acid, along with the picric acid, is sent to a centrifuge or Nutsch filter.

The further treatment is identical with that described in our heading "Production of Picric Acid from Phenol".

In Germany, nitration of chlorobenzene is performed in two stages in batch-type apparatus. After the dinitrochlorobenzene has been produced, the spent acid is utilized in its entirety for nitration of chlorobenzene. After nitration of the chlorobenzene, the spent acid is extracted by the latter, and goes to denitration and concentration. The consumption data per ton of dinitrophenol are: 1.2 ton dinitrochlorobenzene, 0.43 ton caustic soda, and 0.26 ton sulfuric acid.

Nitration of dinitrophenol is performed in batch-type apparatus. 96 - 98% Sulfuric acid, and dinitrophenol, are run into the apparatus (bath /module 3:1) subsequent to which mixed acid consisting of 51% H_2SO_4 and 49% HNO_3 is run in

gradually at 45°. Upon the conclusion of nitration, the reaction mixture is diluted with water, and the picric acid is separated from the dilute spent acid on a suction filter. The picric acid is then washed with water and dried on a rack desiccator. In order to extract picric acid from the spent acid, it undergoes chlorobenzene extraction and then goes to denitration. The chlorobenzene employed for extraction is treated with a soda solution to remove picric acid therefrom in the form of sodium picrate.

The consumption data per ton of picric acid are: 0.86 ton dinitrochlorobenzene, 2.85 ton sulfuric acid, 0.36 ton nitric acid, and 0.05 ton chlorobenzene.

Section 4. Nitrophenol Ethers

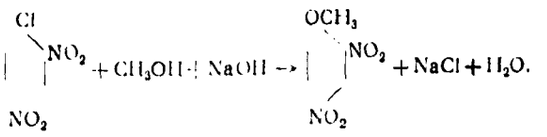
The desirability of employing ethers and in particular di- and tri-anisole and phenetole is dictated by the possibility offered to employ them to make ammonium nitrate explosives. Di- and trinitrophenols are unsuited to this purpose, as they react with the nitrate to form nitric acid. The ethers of the di- and trinitrophenols are less sensitive, but more powerful explosives than are the responding nitrophenols. Like the ethers, they are capable of undergoing hydrolysis (even with water) to form the corresponding phenols and alcohols. Hydrolysis goes the more easily, the larger the number of nitro groups in the nitro ether.

The most important of the nitro derivatives of ethers is phenol dinitroanisole $C_6H_3(NO_2)_2OCH_3$, the production of which attained 300 tons per month in Germany in 1944.

Dinitroanisole is a crystalline substance that exists in two modifications,

one of which has a freezing point of 86.9° , and the other 95°. Its heat of formation is 46.42 kcal/mole (Bibl.216). Dinitroanisole dissolves in water with difficulty, better in alcohol and ether, and very well in acetone and benzene. The following are the explosive characteristics of dinitroanisole. The volume of gaseous products of explosion is 726 ltr/kg, the
204 velocity of detonation is 5620 m/sec, and the fugacity is 245 cc.

Dinitroanisole is produced by the treatment of dinitrochlorobenzene with caustic soda in the presence of methyl alcohol, in accordance with the reaction:



The NaOH solution is added to the mixture of dinitrochlorobenzene and methyl alcohol at 18 - 20°, with a rise in temperature to 45°. After cooling, the dinitroanisole is filtered, washed, and dried. The yield is about 94% of theoretical.

A method of direct nitration of anisole has also been described (Bibl.217).

Dinitroanisole is employed as one of the components in the manufacture of powders with a non-volatile solvent.

Trinitroanisole: 2,4,6-trinitroanisole $C_6H_2(NO_2)_3OCH_3$ is a crystalline substance with a melting point of 68.4°. It has somewhat greater brisance than TNT, but less than picric acid. The volume of gaseous explosion product is 740 ltr/kg, and the fugacity is 314 cc.

Trinitroanisole was produced on a rather large scale in Japan during World War II. It was employed in mixtures with RDX (60% trinitroanisole, 40% RDX) and with hexyl (60% trinitroanisole, 23% hexyl, and 16% aluminum). A mixture of 70% trinitroanisole and 30% aluminum was employed in naval incendiary shells (Bibl.188).

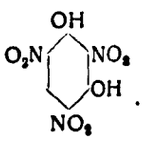
2,4,6-Trinitrophenetole $C_6H_2(NO_2)_3OC_2H_5$ is a crystalline substance with a melting point of 81°. The brisance of trinitrophenetole is less than that of TNT.

Trinitroanisole and trinitrophenetole are produced by nitrating the corresponding dinitro derivatives, which in turn, are obtained from dinitrochlorobenzene and the corresponding alcohol, in the presence of caustic soda (Bibl.218).

A considerable advantage enjoyed by these ethers over picric acid is their neutrality, making it possible to employ them in a mixture with ammonium nitrate. However, as has been pointed out by A.G.Gorst (Bibl.219), the employment of these mixtures during World War I showed that, in the presence of moisture, the ethers undergo hydrolysis to convert to picric acid and alcohol.

Section 5. Trinitroresorcinol (Bibl.208, 220)

Trinitroresorcinol was first obtained in 1808 by Chevreul. In 1946 Boettger and Ville again obtained this substance, and called it styphnic acid. In 1871, Stenhouse and Schroeder showed that styphnic acid is a product of the nitration of resorcinol, and has the following formula



to produce
Trinitroresorcinol is employed/sodium trinitroresorcinate (TNRS), which is an initiator.

205 Trinitroresorcinol (2,4,6-trinitro-1,3-dicxybenzene) consists of bright yellow crystals of the hexagonal system. Its specific gravity is 1.83, and melting point 180°. This product is weakly soluble in water: at 14°, only 0.65% dissolves, and at 62°, 1.1%. The solubility in various solvents is shown in Table 71.

Table 71

a)	b)				
	0	5	10	17	68
Alcohol	5,10	—	—	6,22	14,65
Benzene	—	4,5	—	—	47
Toluene	—	—	5,1	—	—
Acetone	—	—	—	313,1	—

a) Solvent; b) Solubility of trinitroresorcinol, gm, at temperatures, in °C (in 100 gm solvents)

An aqueous solution of trinitroresorcinol is bright yellow, apparently owing to its dissociation into ions.

Trinitroresorcinol is a rather strong acid and is similar to trinitrophenol in its properties. Being a dibasic acid, it can form neutral and acid salts. Its neutral salts are as stable as the salts of trinitrophenol. A strong aqueous solution of trinitroresorcinol dissolves iron and zinc to liberate hydrogen, and this reaction goes with particular ease upon heating. It does react with copper, sulfur, lead, tin, and cadmium. The carbonates decompose trinitroresorcinol, with liberation of carbon dioxide.

Nitric and sulfuric acids (dilute and strong) do not react with trinitroresorcinol

even upon boiling, but merely dissolve it. Aqua regia, however, oxidizes it to oxalic acid and other products. Trinitroresorcinol is somewhat more powerful explosive than picric acid (Bibl.221). Ignited trinitroresorcinol burns with a bright flame but without explosion. A cap detonator will cause it to explode.

Production of trinitroresorcinol. The initial products for production of trinitroresorcinol are resorcinol, nitric acid, and sulfuric or acetic acid.

Resorcinol (meta-dioxybenzene) $C_6H_4(OH)_2$ is a white crystalline substance. Its specific gravity is 1.272, melting point 110.7°, and boiling point 276,5°.

Table 72 presents the solubility of resorcinol and various solvents.

Table 72

a)	b)				
	0	12	15	24	30
Water	86,4	117	—	—	228
90% Alcohol	—	—	127	—	—
Benzene	—	—	—	2	—

a) Solvent; b) Solubility of resorcinol, gm (in 100 gm solvent); c) temperature, °C

Resorcinol is virtually insoluble in chloroform and carbon disulfide. In the presence of ammonia it takes on a reddish tinge, and in an ammonia solution of silver nitrate, it reduces silver. With aqueous solutions of ferric chloride, resorcinol yields a blue color. When chlorine or bromine react with aqueous solutions of resorcinol, the consequence is trichloro- or tribromoresorcinol. This is the basis for the method of quantitative determination thereof. To an aqueous solution of resorcinol, a titrated solution of bromine water is added

(tribromoresorcinol being obtained), and the excess bromine is determined by back-titration with iodine and hyposulfite.

Resorcinol does not yield a precipitate with lead acetate, but its isomer-pyrocatechinol does form a precipitate.

Resorcinol is obtained from benzene through disulfobenzene as intermediate. The raw resorcinol is purified by vacuum distillation. Depending upon the degree of purification, the technical products may contain homologs and isomers as impurities: phenol, pyrocatechinol, hydroquinone, fluoroglucinol, and diresorcinol. In addition, one also encounters thioresorcinol, organic acids (salicylic and phthalic), resins, and water-insoluble impurities. Resorcinol that has been inadequately purified is brown in color and smells of phenol. Even after careful purification by volitilization, steam distillation, and crystallization, technical resorcinol may still contain phenol and pyrocatechinol.

When technical resorcinol is to be nitrated, the presence of resinous substances, which cause the nitro mixture to foam up (due to oxidation) and reduce the quality of the nitro product, is particularly undesirable. Therefore, special technical requirements must be met by resorcinol, under which its melting point has to be in the 109 - 111° interval, the resorcinol content must be not less than 99%, that of pyrocatechinol not over 0.3%, that of phenol and other brominators must be not more than 0.1%.

Nitration of resorcinol, as that of phenol, can only be performed at low temperature (0 - 5°), and by a weak mixed acid or nitric acid. However, even if these conditions are adhered to, the yield of nitro product is small because

of oxidation.

Considerably smaller losses of resorcinol due to oxidation occur when it is nitrated by a diacetyl derivative. To do this, a finely ground resorcinol is dissolved in glacial acetic acid or in acetic acid chloroanhydride. The result of the reaction is formation of a diacetyl resorcinol solution, which is run into strong nitric acid, accompanied by careful agitation and cooling. Three times the theoretical quantity of nitric acid is employed. After run-in, the reaction mixture is permitted to stand for 3 or 4 hrs, with continued stirring, and with heating from time to time until bubbles begin to be emitted. At the end of the holding time, the mass is poured into five times the quantity of commercial sulfuric acid, with cooling and agitation, and is heated to 60° for 2 hrs. The resultant reddish brown mass is poured into a large amount of water, in which the bright yellow crystals of trinitroresorcinol come down. The product yield is approximately 70% of theoretical.

Today, trinitroresorcinol is obtained through resorcinol sulfonic acid as intermediate, with subsequent nitration of the final product. The yield is 84% of theoretical. The technology is substantially similar to that of the production of picric acid, and consists of the following.

Resorcinol is finely ground in iron drums with cast-iron balls, or on special mills. Commercial sulfuric acid is run from the metering tank into the sulfurate, and the resorcinol is run in batchwise, with the agitator operating. The sulfuric acid has to be five times the theoretical, by weight, in order for disulforesorcinol to be formed. Sulfonation is performed at 35°, and, at the end

of the process, the result is a reddish-violet transparent solution of disulforesorcinol in sulfuric acid. In order to bring the reaction all the way to completion, the sulfo mixture is held for 1 - 1.5 hrs at 60 - 70°, subsequent to which the disulforesorcinol solution is cooled to 30°, and nitration is undertaken.

Therefore, mixed acid is gradually run into the disulforesorcinol in sulfuric acid solution, thus raising the temperature to 37°. At the conclusion of the run-in, formation of trinitroresorcinol crystals begins, as a consequence of which the viscosity of the mass increases, and liberation of nitrogen oxides
207 results in foam formation. If stirring is inadequate, due to foaming, the consequence may be local overheating and sudden changes in temperature. Therefore, particularly careful stirring is necessary at this stage in the process. To do this, a foam-breaker is provided on the agitator. Should there be a sudden jump in temperature, the nitro mixture has to be dumped into the emergency pot. At the conclusion of the run-in, the temperature is raised to 50°, and is then held for an hour at 60 - 65°. Completion of holding is determined by the color of the crystals, which have to be from orange to yellow. The nitro mass is then cooled to 25 - 35°, and drained into a dilution tank filled with water. This operation is accompanied by foaming and increase in temperature, and therefore has to be performed stepwise, to avoid sudden emission of nitrogen oxides and sudden changes in temperature.

Upon dilution, trinitroresorcinol comes down as a precipitate, inasmuch as its solubility in the water is less than in spent acid. The crystals are separated from spent acid in a vacuum funnel, and are washed first with warm water (50°), and then with cold (20°).

When low-grade resorcinol are employed, the trinitroresorcinol is purified by treatment with sodium bicarbonate:

$$C_6H(NO_2)_3(OH)_2 + 2NaHCO_3 \rightarrow C_6H(NO_2)_3(ONa)_2 + 2CO_2 + 2H_2O.$$

Neutralization of sulfuric acid to Na_2SO_4 occurs simultaneous with the above reaction. Further treatment of the solution obtained by nitric acid results in precipitation of pure nitroresorcinol. About 5% of the product is lost in purification. Purification is performed as follows.

The trinitroresorcinol is mixed with 3 - 4 times its weight in water, and a 12.5% sodium bicarbonate solution, in a little more than the theoretical quantity, is run into this mixture in a thin stream at 85 - 90°. The approximately 15% sodium trinitroresorcinol solution obtained is cooled to 40 - 45° and treated with strong nitric acid. The precipitated trinitroresorcinol is refiltered and washed with water. The product yield is about 78% of the theoretical. After purification, it is dried in a rack-type drier at 50 - 60°, for 36 hrs.

The technical product usually contains isomers, mono- and di-nitroresorcinol, as well as a certain amount of H_2SO_4. The trinitroresorcinol employed to produce lead trinitroresorcinate has to satisfy the following conditions: melting point not under 174°, water-insoluble impurities not over 0.5%, ashes not over 1%, and H_2SO_4 not over 0.2%.

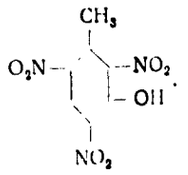
Section 6. Trinitrocresol and Other Nitro Derivatives of Cresol

Trinitrocresol can only be regarded as an auxiliary explosive to be obtained from an extra source of raw material - cresol. It has no particular advantages as

an explosive over picric acid, if we do not consider its lesser degree of solubility in water and lesser reactivity. It is equal to TNT in its explosive qualities.

The starting material - cresol - is hardly suited to nitration in the raw form, as it consists of a mixture of meta-, ortho-, and para-isomers, of which only the meta-cresol yields a trinitro derivative.

208 Trinitro-meta-cresol is a bright yellow crystalline substance melting at 109.5°. Its formula is



A trinitro-meta-cresol of 1.64 density may be produced by pressing and pouring. It dissolves in water less readily than does picric acid. Thus, 100 parts water by weight will dissolve (in parts by weight)

at 6°	0,15
at 25°	0,20
at 100°	1,83

Trinitro-meta-cresol readily dissolves in alcohol, ether, benzene, and acetone. Its chemical properties are similar to those of picric acid. With metals and oxides thereof, it forms cresylates. Cresylates are somewhat less sensitive to shock and heating than are the corresponding picrates. Like the picrates, the most sensitive are the salts of the heavy metals, and the most sensitive of all is the lead salt.

Trinitrocresol is a wholly stable substance, which begins to decompose at about 200°. Its flash point is 2'5°. It is somewhat less shock-sensitive than picric acid, and is inferior thereto in fugacity and brisance. Trauzl bomb expansion is 290 cc, brisance, according to Kast is 4.2 mm, velocity of detonation is 6850 m/sec, volume of gaseous explosion product is 675 ltr/kg, and heat of explosion is 912 kcal/kg.

Trinitrocresol is not employed by itself. In France, it has been employed in alloys with picric acid. The most frequently used was an alloy of 60% trinitrocresol 40% picric acid, called cresolite. A valuable property of this alloy is the fact that it is less sensitive than picric acid, has a low melting point (75 - 80°) and is plastic at 65 - 70°, which makes it possible easily to obtain a dense charge (Δ = 1.65). In Austria, employment was made of an ammonium salt nitrocresol, which has no particular value as an explosive.

Production of trinitrocresol. The starting material for production of trinitrocresol is meta-cresol which is obtained from the neutral oil of coal tar, in a mixture with ortho- and para-cresol. Technical coal cresol is of approximately the following composition: 40% ortho-, 35% meta- and 25% para-isomer. Table 73 presents the properties of cresol isomers.

Table 73

a)	b)	c)
Ortho-	190,8	30
Meta-	202,8	3—4
Para-	202,0	36

a) Cresol isomer; b) Boiling point, °C; c) Melting point, °C

Upon nitration, meta-cresol yields 2,4,6-trinitro-meta-cresol, with a yield of about 80%. Under the conditions of nitration of the meta-isomer, the ortho- and para-cresols undergo complete oxidation with formation of oxalic acid.

Nitration thereof at low temperature makes it possible to obtain the

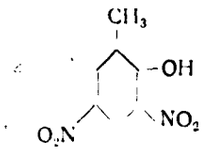
209 trinitro derivatives, which are, however, so unstable as to decompose even under the effect of cold water. Therefore, before technical cresol may be used for nitration, it is distilled, to separate the ortho-isomer, the para- and meta-isomer remaining in the mixture, inasmuch as their boiling points are quite similar. The so-called technical meta-cresol, thus liberated, contains about 40% para-cresol.

Further separation of these isomers may be achieved by oleum treatment of technical meta-cresol. The result is that the para-cresol goes into a crystalline sulfo compound, poorly soluble in acid, and the meta-cresol goes into a sulfo compound readily soluble in acid. The crystals of the para-cresol sulfo compound are filtered off, and the solution of the sulfo compound of meta-cresol in sulfuric acid are nitrated, to yield trinitro-meta-cresol.

Nitration may be employed to obtain the dinitro derivative from the sulfur derivative of para-cresol, or , by live-steam treatment, to recover the initial para-cresol. However, it is more economical to use technical meta-cresol in nitration, without separating the para-isomer.

The technical process of production of trinitrocresol is similar to that involved in obtaining nitric acid from phenol. The yield of trinitrocresol is about 50% of the theoretical. This low yield is explained by the oxidation of para-cresol.

In recent years, considerable interest has developed in 3,5-dinitro-ortho-cresol



209 as a product of considerable herbicidal activity. This product may be produced ~~by~~ via the disulfo derivative of ortho-cresol, for example, by saturating it with an aqueous solution of nitrogen oxides (Bibl.222).

Not long ago, a patent has been published (Bibl.223) for a continuous method of producing dinitro-ortho-cresol, in accordance with which 12.9 kg ortho-cresol and 34 kg 70% nitric acid are admitted, in the course of an hour, through a calibrated nozzle, into a water-cooled metallic tube 1 m long and 38 mm in diameter. The yield of dinitro-ortho-cresol was 80% of the theoretical.

209

CHAPTER VI

NITRO COMPOUNDS OF THE ALIPHATIC SERIES

A. General Description

The nitro compounds of the aliphatic series (nitro paraffins, nitro alkanes) have come into wide use in the last 10 - 15 years as components of jet fuels. Because of their high reactivity, they may be employed as the starting materials for the production of a number of valuable chemicals, acids, amines, nitroalcohols, etc., as well as for the synthesis of powerful explosives. The problem of obtaining and utilizing nitro compounds of the aliphatic series for these purposes is also important because a cheap and large supply of raw materials for them is available, inasmuch as paraffins are a basic component of petroleum, industrial, and natural gas.

210 The nitroalkanes were obtained in 1872 by V.Meyer by reacting silver nitrite with alkyl iodides:

$$C_nH_{(2n+1)}J + AgNO_2 \rightarrow C_nH_{(2n+1)}NO_2 + AgJ.$$

Subsequently, this reaction came to be performed by reacting nitrite salts of other metals with sulfuric esters, for example:

$$\begin{matrix} CH_3O \\ CH_3O \end{matrix}\!\!\diagdown SO_2 + KNO_2 \rightarrow CH_3-NO_2 + CH_3OSO_2OK.$$

The reaction product included not only nitro compounds, but nitric esters (for example, CH_3ONO), and, because of their lower boiling point, these latter were readily separable from the basic product by distillation.

Formation of nitro compounds as a result of the reaction of nitrite having a tri-valent nitrogen atom, is explained by the fact that, along with the exchange reaction, leading to the formation of nitric esters, there is a halide alkyl

210 addition reaction, followed by the cleaving off of a halide salt:

$$Ag^{\oplus}[O^{e}-N-O]+CH_3-J \rightarrow \left[Ag-O-N^{\oplus}\begin{matrix}\diagup O \\ \diagdown CH_3\end{matrix}\right]J^{e} \rightarrow$$

$$\rightarrow AgJ+O^{e}-N\begin{matrix}\diagup\!\!\!\diagup O \\ \diagdown CH_3\end{matrix} \quad \left(\text{or} \quad O \leftarrow N\begin{matrix}\diagup O \\ \diagdown CH_3\end{matrix}\right).$$

The obtaining of nitroalkanes by means of $AgNO_2$ is of significance only in the laboratory. Running this reaction in a medium dimethylsulfoxide or dimethylformide, containing urea, makes it possible to employ $NaNO_2$ instead of $AgNO_2$. When this is done, the yield of primary and secondary nitroalkanes attain 60% (Bibl.1, 2).

Twenty years later, in 1892, M.I.Konovalov obtained nitroparaffins by direct reaction of nitric acid (10 - 15% strength) with liquid saturated hydrocarbons: pentane, hexane, etc., at temperatures in the vicinity of 115 - 150°. Considerably later, A.I.Titov, investigating this reaction, demonstrated, (Bibl.3), that the active chemical agent therein is a molecule of the monomer of nitrogen dioxide, similar to a radical, and regenerated from nitric acid.

Reaction of the nitrogen dioxide monomer with paraffin hydrocarbons results in the formation of radicals

$$R:H+\cdot NO_2 \rightarrow R\cdot + HNO_2,$$

which combine with extreme rapidity with the next molecule of the nitrogen dioxide monomer

$$R\cdot + \cdot NO_2 \rightarrow R-NO_2.$$

Simultaneously, the regeneration of $\cdot NO_2$ occurs

$$HNO_2+HNO_3 \rightarrow H_2O+2\cdot NO_2.$$

Formation of nitric esters is also possible as side products:

210

$$\cdot NO_2 \rightarrow \cdot O-NO;$$
$$R\cdot + \cdot O-NO \rightarrow R-ONO.$$

211 These latter go into a series of reactions, reversible in nature, such as hydrolysis

$$R-ONO + H_2O \rightleftarrows ROH + HONO$$

and other transformations.

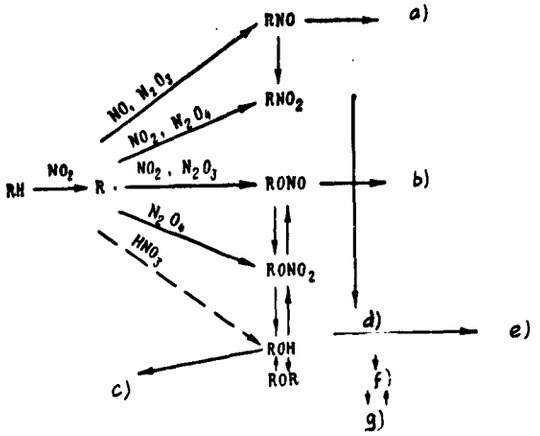
To be noted that the ease with which substitution by the nitro group occurs increases as one proceeds from the primary hydrogen (in the CH_3 group) to the secondary (in the $=CH_2$ group). The substitution of the ternary hydrogen goes easiest of all (in the group $\equiv CH$).

When nitric acid is reacted with paraffin hydrocarbons, oxidation products (Bibl.4) are produced in significant quantity simultaneous with the nitration product. The yield of these oxidation products not infrequently exceeds the yield of the nitro compounds, particularly if the process is run at high temperature, inasmuch as the temperature coefficient of the oxidation reaction is higher than that of the nitration reaction.

It is proposed that nitrogen dioxide be employed to [illegible] nitrate paraffin hydrocarbons instead of nitric [illegible] acid. This process is run in liquid phase at 150 - 200° at 20 atm pressure (Bibl.5,6).

A.I.Titov expresses the mechanism of formation of oxidation products in the nitration of paraffin hydrocarbons as follows (Bibl.3):

[illegible]



a) Oxines and other conversion products; b) Lower radicals, ketones, aldehydes, and their conversion products; c) Olefines and their conversion products; d) Ketones aldehydes; e) Lower acids, nitriles, HCN, oxy acids, etc.; f) Acids; g) Esters

Nitration of paraffin hydrocarbons in the liquid phase is rendered difficult by the fact that the hydrocarbons and the nitric acid are mutually insoluble, and, moreover, the resultant nitro product is partially soluble in nitric acid, with the consequence that it undergoes further nitration and oxidation.

In 1936 and 1937, studies appeared on the nitration of pentanes and butanes in the gaseous phase by nitric acid of 1.5 specific gravity. According to the data of Bachman (Pi-1.7,8,9), this process goes better in the presence of halides or oxygen, which facilitate the formation of low-molecular nitro paraffins. The mechanism by which these additives operate consists of the formation of free hydrocarbon radicals arising through the reaction of the hydrocarbon with the halide or oxygen. Moreover, the halides take up the nitrogen oxide, and prevent nitration.

211 In the gaseous phase, the reactants are miscible in any proportion. The essence of the production lies in the fact that the hydrocarbon vapors are passed through a coil reactor, into which hot, strong nitric acid is admitted simultaneously. Passed the coil reactor, the mixture of hydrocarbon and nitric acid fumes passes through a

212 reaction apparatus in which a temperature of 400 - 450° is maintained. As a consequence, the free radicals formed at high temperature (Bibl.9) participate in the reaction. Thus, [illegible] first [illegible] a process of decomposition of paraffin hydrocarbons into free radicals: R - R $\rightarrow$ 2R·, and then subsequent combination thereof with a decomposition product of nitric acid: NO, NO_2, H_2O, into nitroso-, nitro-, and oxyparaffins.

At a temperature of 400 - 450°, derivatives of the lower hydrocarbons are obtained from the higher paraffin-[illegible] hydrocarbons. However, if the process be run at a temperature under 350°, cracking of the paraffins [illegible] does not occur, and formation of products of nitration and oxidation of the hydrocarbons taken for nitration occurs.

For the explosives industry, it is only the nitro derivatives of the lower hydrocarbon paraffins that are of interest: nitromethane and nitroethane. The latter may be obtained by [illegible] vapor-phase nitration at 400 - 450°, from the higher paraffinic hydrocarbons, constituting a component of petroleum (Bibl.10, 11). The ratio of the components is of importance in connection with process safety. When the HNO_3-to-hydrocarbon ratio [illegible] is 8:1, one obtains a stoichiometric ratio of combustible and oxidizer, constituting and explosive mixture. Therefore, the process is run with mixtures containing excess hydrocarbon (from 2.5 to 10 parts by weight per part HNO_3 by weight). This simultaneously facilitates an increase in the yield of nitration products.

212 In nitration in the vapor phase, more than 60% of HNO_3 is consumed in oxidizing processes, in which it is reduced to nitrogen oxides. The nitrogen oxides are sent to absorbers to recover nitric acid. This significantly reduces the dead losses thereof, and the degree of loss is governed solely by the completeness of which the apparatus is sealed.

The resultant nitroparaffins must immediately be removed from the high-temperature zone, and cooled, to prevent decomposition thereof. The temperature and time of contact of hydrocarbons with HNO_3 are interdependent. The higher the temperature, the less must be the contact time. For example, for pentane at 450°, 0.22 sec contact time is adequate, at 398°, 1.0 sec. will do, and 366° - 2.9 sec, and at 248° - 852 sec.

The optimum temperature for the various hydrocarbons differs and is determined by their stability. The more difficult it is for a hydrocarbon to be cracked, the higher must be the temperature of nitration in the vapor phase. Thus, for example, the optimum nitration temperature of methane is 550 - 600°, that of ethane is 500 - 550°, propane - 410 - 450°. butane - 380 - 410°.

The optimum temperature drops with increase in the molecular weight of the hydrocarbon, and with branching of the carbon chain. Hydrocarbons of larger molecular weight, and, molecular weight being equal, isomeric hydrocarbons, crack more readily. Pressure, which does not affect the nature of vapor-phase nitration, has a major effect upon its velocity, inasmuch as an increase in pressure is accompanied by an increase in the volumetric concentration of the components. This makes it possible to reduce the contact temperature and time. Nitration is usually performed at 7 - 10 atm. There are also installations that function at atmospheric pressure.

Installations functioning under pressure are more compact, and the reaction goes

XXX

212 at lower temperature, however this requires absolute airtightness of apparatus (Bibl.5,10).

The iron walls of the apparatus are inhibitors of vapor-phase nitration and sharply diminish the yield of nitroparaffins. The introduction of KNO_3 or $NaNO_3$ into the apparatus makes it possible to reduce this effect somewhat (Bibl.9).

In the USA, gas-phase nitration is performed in reactors of chrome-nickel steel. The metering and delivery of the components is automatic. They are preheated by passing through heat exchangers or tubular furnaces. The residence time

213 of the mixture in the reactor is regulated by the rate of component delivery.

The mixture goes from the reactor to a condenser. The distance between reactor and condenser should be minimal so as to assure rapid cooling of the nitroparaffins and prevent decomposition thereof. Cooling is performed stepwise. High-boiling fractions condense in one condenser, and low-boiling in another. These fractions go to preliminary distillation, subsequent to which each fraction is subjected to chemical purification and is again distilled in a fractional distillation apparatus.

Figure 64 shows a schematic diagram of the apparatus for gas-phase nitration.

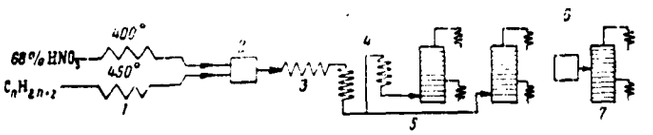


Fig.64 - Diagram of Apparatus for Gas-Phase Nitration of Aliphatic Hydrocarbons
1 - Heater; 2 - Mixer; 3 - Reactor; 4 - Condenser; 5 - Preliminary distillation; 6 - Chemical purification; 7 - Distillation

In some apparatus, the nitric acid is not heated to high temperature (of the order

213 of 250 - 400°) but is merely vaporized. This prevents deep decomposition to NO and O_2.

A number of indirect methods of producing nitroparaffins (Bibl.12,13,14) are also known:

1) oxidation of amines in accordance with the following mechanism

$$2RCH_2NH_2 \xrightarrow{O_2} 2RCH_2NHOH \xrightarrow[-2H_2O]{O_2} 2RCH{=}NOH \xrightarrow{O_2} 2RCH_2NO_2.$$

The yield of nitroparaffins is 30 - 50%. Nitrocompounds are formed upon the oxidation of the primary amines only. Oxidation does not cause the secondary and ternary amines to yield nitro derivatives. Reaction of olefins with nitrogen tetroxide goes as follows:

$$2(CH_3)_2C{=}C(CH_3)_2 + 2N_2O_4 \begin{cases} \nearrow (CH_3)_2C(NO_2)-C(NO_2)(CH_3)_2 \\ \searrow (CH_3)_2C(ONO)-C(NO_2)(CH_3)_2 \end{cases}$$

The dinitro compound constitutes 30 - 50% of the mixture, while the residue consists of nitroalkyl nitrite. This latter has a tendency to spontaneous decomposition, which is responsible for the instability of the resultant reaction mixture;

2) reaction of ketones with nitric esters (Bibl.15) or with hydroxylamine, followed by reacting nitrogen and an oxidizer (a chromium mixture or nitric acid) with resultant oxime in accordance with the following mechanism

$$\underset{CH_3}{\overset{CH_3}{>}}C{=}O \xrightarrow[-H_2O]{+NH_2OH} \underset{CH_3}{\overset{CH_3}{>}}C{=}NOH \xrightarrow[-HNO_2]{+N_2O_4} \underset{CH_3}{\overset{CH_3}{>}}C(NO)(NO_2) \xrightarrow{+O} \underset{CH_3}{\overset{CH_3}{>}}C(NO_2)_2$$

The yield of dinitro compound is 25 - 35%.

3) permanganate oxidation of ternary carbinamines is employed to obtain ternary nitro compounds, the yield being 70 - 80% (Bibl.16).

Properties of nitroparaffins (Bibl.17). Mononitroparaffins are colorless liquid

213 or solid substances. [illegible]

Table 74 shows the physical properties of mononitroparaffins, from which it is clear that, as the molecular weight [illegible] of mononitroparaffins rises, their boiling point increases, and their specific gravity diminishes.

Mononitroparaffins are poorly soluble in water. Thus, 10.5 cc nitromethane dissolves in 100 cc water at 100°. The solubility of the residual members of the

214 homologous [illegible] series diminishes as molecular weight rises. The mononitroparaffins are readily soluble in benzene, toluene, xylene, alcohol, acetone, and carbonic acid. The lower nitroparaffins are themselves solvents for many organic substances.

Table 74

a)	b)	c)	d)	e)
Nitromethane	CH_3-NO_2	101,2	1,132	1,3935 (at 20°)
Nitroethane	$CH_3-CH_2-NO_2$	114,0	1,047	1,3901 (at 24°)
1-Nitropropane	$CH_3-CH_2-CH_2-NO_2$	131,6	1,008	1,4003 (at 24°)
2-Nitropropane	$CH_3-\underset{\underset{NO_2}{\vert}}{CH}-CH_3$	120,8	1,024	—
1-Nitrobutane	$CH_3-(CH_2)_2CH_2NO_2$	152,9	—	—
2-Nitrobutane	$CH_3-CH_2-\underset{\underset{NO_2}{\vert}}{CH}-CH_3$	139,6	0,988	—
1-Nitro-2-methylpropane	$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH-CH_2-NO_2$	137—140	—	—
2-Nitro-2-methylpropane	$CH_3-\underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}-NO_2$	126,5	—	—
1-Nitropentane	$CH_3-(CH_2)_3-CH_2-NO_2$	172—173	0,948	1,4218 (at 20°)
1-Nitrohexane	$CH_3-(CH_2)_4-CH_2-NO_2$	193—194	0,949	—

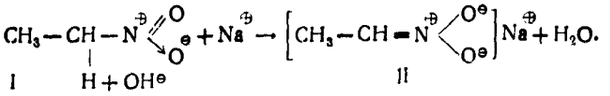
a) Compound; b) Formula; c) Boiling point, °C; d) Specific gravity at 15°; e) Refractive index

[illegible]

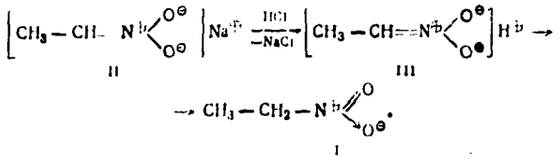
214 Dinitroparaffins are colorless, and in a majority of cases crystalline substances, insoluble in water, and readily soluble in organic solvents.

In the primary and secondary nitro compounds, the hydrogen, standing near the carbon, bound to the nitro group, is mobile, and therefore these nitro compounds are capable of undergoing a number of reactions characteristic thereof. They react with aqueous solutions of caustic alkalis, forming water-soluble compounds with the properties of neutral salts. These substances are aci salts of the isonitro compounds, and constitute strong acids.

Reaction of nitro compounds with alkalis follows this mechanism:



215 The fact that the neutral nitro compounds are isomerized to acid isonitro compounds is confirmed by the fact that when strong acid reacts with an isonitro compound salt (II) the water-insoluble nitro compound (I) is not obtained immediately. First, the isonitro compound (III), which is readily soluble in water, is liberated, and it undergoes conversion to nitro compound (I) only gradually:



It has not been possible to isolate the simplest isonitro compounds in the pure form, because their conversion into true nitro compounds occurs very rapidly.

It is possible to replace one hydrogen atom in the secondary nitro compounds, and one or two hydrogen atoms in the primary nitro compounds by halide atoms, as a

215 consequence of reacting halogens with alkaline solutions of the nitro compounds. This results in the following compounds:

$$R-CHBr-NO_2;\quad R-CBr_2-NO_2;\quad \begin{matrix} R \\ R' \end{matrix}\!\!>\!CBr-NO_2.$$

The reaction with nitrous acid is characteristic and permits differentiation of the primary, secondary and ternary nitro compounds:

a) the primary nitro compounds react with nitrous acid to form so-called nitrolic acids:

$$R\cdot CH_2-NO_2+ON-OH \rightarrow R-C\begin{matrix} NOH \\ NO_2 \end{matrix}+H_2O.$$

The alkaline salts of nitrolic acids are bright red;

b) the secondary nitro compounds react with nitrous acid to form so-called pseudonitrols:

$$\begin{matrix} R \\ R' \end{matrix}\!\!>\!CH-NO_2+HO-NO \rightarrow \begin{matrix} R \\ R' \end{matrix}\!\!>\!C\begin{matrix} NO \\ NO_2 \end{matrix}+H_2O.$$

In the crystalline state, these substances are colorless, but in the fused condition and in solutions (in ether, chloroform, etc.) they have a bright turquoise coloration;

c) the ternary nitro compounds do not react with nitrous acid.

Reduction of the nitro compounds results in the formation of the primary amines:

$$CH_3-NO_2+6H \rightarrow CH_3-NH_2+2H_2O.$$

This reaction shows that in nitro compounds, the nitrogen atom is directly bound to the carbon atom. On the contrary, in reduction of isomeric nitro compounds of nitrous esters, in which an alkyl is bound to oxygen, one obtains alcohol or ammonia

215 or hydroxylamine:

$$CH_3-O-N=O+4H \rightarrow CH_3OH+NH_2OH.$$

The products of reduction of nitro compounds in an alkaline medium are aldoximes and ketoximes. It is probable that the isonitro compound is reduced in these cases:

$$R\cdot CH-NO-OH+2H \rightarrow R-CH=N-OH+H_2O.$$

Under conditions of reduction by tin and hydrochloric acid, oximes are capable of being hydrolized, and decomposed to form hydroxylamines and aldehydes or ketones.

216 The primary and secondary nitro compounds enter into condensation reactions with the aldehydes under the influence of alkalis, to yield nitro alcohols (Bibl.18), for example:

$$R-CH-O+CH_3-NO_2 \rightarrow R-CH(OH)-CH_2-NO_2.$$

Under specific conditions (acid reactions), the nitro alcohol obtained may be converted to a nitro-olefin;

$$R-CH=CHNO_2.$$

Primary nitroparaffins condense more readily than secondary.

B. Major Nitroparaffins.

Section 1. Nitromethane

Nitromethane CH_3NO_2 has recently found application in a number of countries as a rocket-fuel component and as an additive to diesel fuel. Its use has been suggested as a solvent for cellulose nitrates and as an explosive in explosive drilling operations in petroleum recovery. It may be employed as a starting product to produce chloropicrin (CCl_3NO_2), tetranitromethane, and a number of explosives.

216 Nitromethane is a colorless liquid, boiling point 101°, freezing point -29° (Bibl.19, 20). Table 75 illustrates the specific gravity and viscosity of nitromethane at various temperatures.

Table 75

a)	b)	c)
10	1,1490	0,748
25	1,1287	0,625
40	1,1080	0,533

a) Temperature, °C; b) Density, gm/cm^3; c) Ostwald viscosity

The thermal capacity of nitromethane at 20° is c_p = 2.07 cal/mole/°C.

Nitromethane is soluble in water (about 9%, at 20°), and itself dissolves 2.2% water. It is miscible with virtually all organic liquids, and is a good solvent for many organic and inorganic substances, including cellulose esters and certain resins.

Nitromethane is a reactive substance. Caustic alkalis induce a peculiar condensation of two molecules thereof, leading to the formation of methazonic acid:

$$2CH_3NO_2 + 2KOH \rightarrow \begin{matrix} O \\ KO \end{matrix}\!\!\gg N{=}CH{-}CH{=}NOK + 3H_2O.$$

Nitromethane and excess formaldehyde forms triatomic alcohol:

$$3CH_2O + CH_3{-}NO_2 \rightarrow (HC{-}CH_2)_3C{-}NO_2.$$

Upon esterification by nitric acid, this alcohol will, like glycerol, yield a trinitrate $(O_2N - O - CH_2)3C - NO_2$ - which is a very powerful explosive.

Nitromethane is an explosive having a negative oxygen balance. Its brisance, according to Hess, is 25 mm(with an auxiliary TNT cap of 5 - 8 gm). The fugacity in the Trauzl block is 470 cc. Shock sensitivity is as follows: the dropping of a 10 kg weight from a height of 25 cm yields 0 - 8% explosion. Velocity of detonation is 6600 m/sec (Bibl.21).

216 Nitromethane is a toxic substance (Bibl.22).

Nitromethane is obtained on an industrial scale in vapor-phase nitration of paraffin hydrocarbons, and also by a number of indirect methods (Bibl.23, 24). Direct

217 nitration of methane has not yet been performed on an industrial scale. Nitration of methane by nitric acid in the gas phase under laboratory conditions provides a nitromethane yield of about 25%.

Of the method of producing nitroparaffins described above, the method involving the production of nitromethane from dimethylsulfate is of practical significance:

$$O_2S\begin{matrix}OCH_3\\OCH_3\end{matrix} + 2NaNO_2 \rightarrow 2CH_3-NO_2 + Na_2SO_4.$$

which gives a yield of about 60%. The reaction is run in an aqueous solution, first at 60°, and then at 120°, in the presence of small amounts of K_2CO_3 (Bibl.25).

Nitromethane may also be obtained by reacting chloroacetic acid with potassium nitrite or sodium nitrite in aqueous solution. The nitroacetic acid resulting therefrom decomposes upon boiling with water:

$$CH_2Cl-COOH + NaNO_2 \rightarrow \underset{NO_2}{CH_2-COOH} \rightarrow CH_3NO_2 + CO_2.$$

Section 2. Dinitromethane

Dinitromethane $CH_2(NO_2)_2$ was first obtained in 1893 by Duden (Bibl.26). Thanks to its exceedingly high reactivity and the presence of two mobile hydrogen atoms, it is able to serve as the basis for the production of polynitro compounds.

Dinitromethane is a colorless, free-flowing and volatile liquid with a characteristic sharp odor, recalling that of methanoic acid. It is stable only at low temperature, whereas at room temperature it decomposes within a few minutes to liberate nitrogen oxide (Bibl.26).

217 Dinitromethane may be driven over without decomposition only with benzene vapors. It is virtually insoluble in cold water but rather soluble in warm water (Bibl.28). Ether and benzene solutions are stable and may be stored for a long time (Bibl.26).

Studies of the absorption spectra (Bibl.29, 30) and the electrical conductivity of aqueous solutions (Bibl.27) have shown that dinitromethane may exist in two tautomeric forms:

$$\underset{\text{I}}{CH_2(NO_2)_2} \rightleftarrows \underset{\text{II}}{NO_2CH{=}NOOH}.$$

Free colorless dinitromethane is a true nitro compound (I). In anhydrous unpolarized organic solvents (benzene, ether), dinitromethane also exists in the form of a true nitro compound, in which case the solutions are colorless.

Dinitromethane has a tendency to convert to the acy form (II), solutions of which are yellow. Conversion of dinitromethane goes more rapidly when water is added. In aqueous solution, dinitromethane is a monobasic acid, similar in strength to methanoic acid. The dissociation constant of the acy form of dinitromethane is $1.43 \cdot 10^{-4}$ at 0° and $2.78 \cdot 10^{-4}$ at 25°. In aqueous solutions of dinitromethane, equilibrium exists between the true nitro compound and the acy form. In very dilute solutions, this equilibrium is wholly shifted to the acy form:

$$H_2C(NO_2)_2 \rightleftarrows NO_2CH{=}NOOH \rightleftarrows NO_2CH{=}NOO^{\ominus} + H^{\oplus}.$$

When alkali is added, the equilibrium is shifted to formation of the acy form, and when acid is added, in the direction of the true nitro compound. In a strong
218 sulfuric acid solution, dinitromethane exists only as the true nitro compound.(Bibl.30, 31).

In its chemical character, dinitromethane is a rather powerful monobasic acid. An aqueous solution thereof yields an acid reaction to litmus paper and to methylorange.

218 In the presence of dinitromethane, free iodine is liberated from a mixture of potassium iodide and iodate (Bibl.27). Dinitromethane decomposes salts of carbonic, sulfuric, and nitrous acids.(Bibl.26). It readily forms salts with inorganic and organic bases, for example, when mixed with ammonium, barium, and copper carbonates or hydroxides with dinitromethane in ether solution. An aqueous solution of its potassium salt yields a neutral reaction. The completely pure potassium salt is stable and may be stored in the open air for a long time.

Salts of dinitromethane explode when heated to over 100°. When dinitromethane is reduced in an acid medium, ammonia is liberated, but if reduction is performed in water by a sodium amalgam, the result is so-called methylazouronic acid - a crystalline substance that explodes at 98°.

When dinitromethane is treated with bromine water, it converts to dibromodinitromethane (Bibl.26). The effect of free halides upon the potassium salt of dinitromethane in the presence of caustic results in the formation of potassiumhalidedinitromethane (Bibl.32). However, if potassiumdinitromethane be treated with excess bromine in neutral solution, bromodinitromethane is formed (Bibl.33).

Dinitromethane readily reacts by condensation with formaldehyde and amines to form dinitroamines. It is capable of attaching to activated double bonds. Usually, the potassium salt of dinitromethane is employed for this type of reaction.

Dinitromethane is obtained by acidification of an aqueous solution of its potassium salt, accompanied by cooling. This latter is obtained in turn from the more accessible organic compounds, for example, dibromodinitromethane: $Br_2C(NO_2)_2$. Dinitromethane may also be obtained from symmetrical dipotassiumtetranitroethane:

$$KOON{=}C(NO_2){-}C(NO_2){=}NOOK \xrightarrow{H_2SO_4} 2CH_2(NO_2)_2.$$

218 Section 3. Trinitromethane

Trinitromethane $CH(NO_2)_3$ (nitroform) was first obtained in 1857 by L.N.Shishkov (Bibl.34). In view of the exceedingly high reactivity, it is capable of being widely used for the synthesis of polynitrocompounds. With this object, nitroform or a salt thereof is condensed with nitro compounds or aldehyde. Condensation with aldehydes results in the formation of nitro alcohols, the nitrates of which are powerful explosives.

Pure anhydrous nitroform is a colorless crystalline substance having a characteristically sharp odor. The melting point is not exactly known, but it is apparently in the range of 23 - 25° (Bibl.19, 35). The boiling point is 45 - 47° at 22 mm Hg (Bibl.36). The specific gravity is $d_{4^\circ}^{25^\circ} = 1.61$ (Bibl.18).

Nitroform readily absorbs moisture, and acquires a yellow color as a consequence. It is readily soluble in water and in the common organic solvents. Solutions of nitroform in water, alcohol, acetic acid, and aqueous ether are yellow. Solutions in
219 anhydrous benzene, chloroform, carbondisulfide, ligroin, ether, and in strong sulfuric or hydrochloric acids, are colorless (Bibl.37). The yellow color relates to isomerization of the nitroform to the acy form:

$$\underset{\mathrm{I}}{H\cdot C(NO_2)_3} \rightleftarrows \underset{\mathrm{II}}{(NO_2)_2C}-N\begin{matrix}\nearrow O \\ \searrow OH\end{matrix}.$$

In aqueous, mildly acid, and basic media, the nitroform exists in the acy form. (II), while in a medium of very strong H_2SO_4, HNO_3, and other acids, as well as in the anhydrous condition, it exists in the form of nitro compound (I). The nitroform explodes when rapidly heated. An attempt to drive it off at atmospheric pressure results in decomposition at 100° (Bibl.34). The Nitroform may be distilled without decomposition. Under ordinary circumstances, it is relatively stable, and may be preserved without undergoing change, in the cold. Strong mineral acids decompose the nitroform (Bibl.34,37).

219 The nitroform is a very strong acid (Bibl.37). It readily forms salts with inorganic and organic bases. All these salts are substances light-yellow in color. They lack odor and have little stability in the dry condition. Inorganic salts decompose after a few hours, converting to nitrates in accordance with the equation:

$$2(NO_2)_2C{=}NOOMe \rightarrow 2MeNO_3 + 2CO_2 + 2NO + N_2.$$

Solution of these salts in water is not accompanied even by the slightest signs of hydrolysis. The resultant yellow solutions have a neutral reaction.

The potassium, ammonia, and sodium salts of nitroform are obtained by reacting a weak solution of alkali with tetranitromethane in the presence of a reducing agent. This is a side process of the formation of the carbonate. The reaction goes as follows:

$$C(NO_2)_4 + 2KOH \rightarrow (NO_2)_2C{=}NO_2K + KNO_3 + H_2O;$$
$$C(NO_2)_4 + 6KOH \rightarrow 4KNO_2 + K_2CO_3 + 3H_2O.$$

The potassium, sodium, and ammonia salts are derivatives of the acy form and are therefore yellow in aqueous solution.

The silver and mercury salts of the nitroform are tautomeric compounds capable of existing in two forms. Solutions thereof in ether, benzene, and chloroform are colorless. Salts freshly crystallized out of these solutions are also colorless crystals. Solutions in alcohols, acetone, and glacial acetic acid are weakly yellowish. Acqueous solutions are strongly yellow, carry electric current, and are quite acid.

Thus, the hydrogen of the nitroform is capable of being substituted for both in the acy form and in the pseudo form. Reaction with bases results in replacement of the hydrogen not only by metals or organic residues, but also by halides, for

219 example, chlorine, with formation of chloropicrin:

$$C(NO_2)_3H + Cl_2 \rightarrow CCl(NO_2)_3 + HCl,$$

or by nitro group, with formation of tetranitromethane:

$$C(NO_2)_3H + HNO_3 \rightarrow C(NO_2)_4 + H_2O.$$

The nitroform is capable of undergoing condensation. Of particular interest is condensation thereof with formaldehyde, as a consequence of which trinitroethylalcohol is formed:

$$CH(NO_2)_3 + CH_2O \rightarrow (NO_2)_3C - CH_2OH,$$

220 which is a powerful explosive. Because of its hygroscopicity and low stability, it has no practical value.

The nitroform is capable of combining with unsaturated compounds at the double or triple bond. For example, it combines with acetylene as follows:

$$\begin{array}{l} CH \quad CH + CH(NO_2)_3 \xrightarrow{Hg(NO_3)_2} \\ \rightarrow CH_2 \quad CH - C(NO_2)_3 \xrightarrow{CH(NO_2)_3} \begin{cases} (NO_2)_3C \cdot CH_2 - CH_2 \cdot C(NO_2)_3 \\ (NO_2)_3C - CH - C(NO_2)_3 \\ \qquad\qquad\quad CH_3 \end{cases} \end{array} \quad II$$

Its salts, and particularly the silver salt, are capable of condensing with aromatic compounds.

The nitroform is an explosive. It can be detonated by shock or a capsule.

The simplest and most convenient method of producing the nitroform is decomposition of tetranitromethane by an aqueous solution of caustic potash. The reaction follows the following equation:

$$C(NO_2)_4 + KOC_2H_5 \rightarrow KC(NO_2)_3 + C_2H_5ONO_2.$$

Free nitroform is liberated by adding an excess strong sulfuric acid to an aqueous solution of a salt thereof:

$$KC(NO_2)_3 + H_2SO_4 \rightarrow HC(NO_2)_3 + KHSO_4.$$

220 The liberated oily product is extracted with ether. After the ether has been driven off in vacuum, the nitroform remains as a volatile, bad-smelling oil, which, after solidification in a freezing mixture and separation over porous clay, forms virtually colorless crystals that melt at 25°. The next section describes the method of obtaining the nitroform from acetylene.

Section 4. Tetranitromethane

Tetranitromethane $C(NO_2)_4$ was obtained in 1857 by L.N.Shishkov by the nitration of trinitromethane (Bibl.34).

The absence of a dipole moment in tetranitromethane testifies to the symmetrical structure of its molecule. This refutes the hypothesis of certain investigators to the effect that the molecule contains one nitrite group O - NO and three nitro groups - NO_2.

Tetranitromethane contains a considerable amount (about 50%) of active oxygen:

$$C(NO_2)_4 \rightarrow CO_2 + 2N_2 + 3O_2.$$

This property was employed in Germany to make jet fuels on the basis thereof (Bibl.38).

Tetranitromethane is a very free-flowing, volatile, transparent, and colorless liquid with a sharp odor. Its specific gravity is $d_{4^\circ}^{15} = 1.65$ (Bibl.39), its freezing point 14.2° (Bibl.40), its viscosity at 20° is 0.0177 poise (Bibl.42). The technical product freezes at 13.5 - 13.8°. The boiling point of tetranitromethane is 126 -127° (Bibl.41). Upon boiling, it partially decomposes into CO_2 and nitrogen oxides.

Tetranitromethane is not hygroscopic, virtually insoluble in water, glycerol, and other multiatomic alcohols. It is readily soluble in many organic solvents: toluene,

.220 benzene, dichloroethane, etc., When these solutions are cooled below the freezing point of tetranitromethane (below 13.5°), the solubility diminishes sharply, and the product

221 crystallizes out.

Several organic substances such as TNT, paraffin, and naphthalene, are miscible with tetranitromethane in any ratios at temperatures above their melting points. Upon cooling of these mixtures, the substances dissolved crystallize out.

Tetranitromethane is insoluble in sulfuric acid. Nitric acid and tetranitromethane are mutually soluble. At 15°, it dissolves 22 - 24 volumes of 98 - 98.6% HNO_3. As the strength of the HNO_3 diminishes, its solubility diminishes. Tetranitromethane readily dissolves nitrogen oxides, and a mixture of various volumes of these substances has a freezing point of -36° (Bibl.43).

Tetranitromethane is volatile. Even at 0°, there is a perceptible odor reminding one of the nitrogen oxides. It is readily distillable with steam. The fumes have an irritating effect upon the mucuous membrane, cause tearing, running nose, and cough. Continued inhalation of the fumes has a poisonous effect upon the organism. Tetranitromethanes are readily absorbed by activated charcoal.

Pure tetranitromethane presents a neutral reaction. Upon standing it becomes acid due to decomposition. Decomposition proceeds most actively in the presence of water:

$$C(NO_2)_4 \overset{HOH}{\rightleftharpoons} CH(NO_2)_3 + HNO_3$$

The quantity of acid products formed is readily determined by titration with alkali. Both decomposition products: HNO_3 and $CH(NO_2)_3$ are titrated (Bibl.44).

Decomposition of the tetranitromethane usually proceeds to equilibrium at an acidity of about 0.1 - 0.2% in terms of HNO_3. If the acid decomposition products are

221 removed by washing with water, decomposition of the next batch of tetranitromethane will occur, and so forth until the entire product is decomposed.

Tetranitromethane is stable in acid media and may be stored for years in this conditions. Therefore, the technical product is stabilized by acidification with sulfuric acid, or with nitrogen oxides to an acidity of 0.1 - 0.2%. In this form, it may be stored in iron apparatus.

Decomposition of tetranitromethane in an alkaline medium may be expressed by two equations:

$$C(NO_2)_4 + 6KOH \rightarrow K_2CO_3 + 4KNO_2 + 3H_2O;$$
$$C(NO_2)_4 + KOH + C_2H_5OH \rightarrow C(NO_2)_3K + C_2H_5ONO_2 + H_2O.$$

With aqueous solutions of alkalis, what occurs is primarily nitrite decomposition, but with alcohol solutions it is nitroformed. The specific properties of tetranitromethane include its ability to produce a dark discoloration with organic substances containing unsaturated bonds.

Tetranitromethane is a weak explosive, has little sensitivity to shock and to other types of initial impulse. Its explosive properties, computed on the basis of the theoretical decomposition equation, are the following: heat of explosive decomposition - 580 kcal/kg, temperature of explosion 2900°, volume of gaseous explosion products - 470 ltr/kg, velocity of detonation - 6300 m/sec.

Mixtures of tetranitromethane and organic substances are usually explosives. Some of them exceed TNT by 50 to 100% in power. However, such mixtures are highly sensitive and therefore very dangerous to handle.

222 Only substances soluble in tetranitromethane, but which do not react with it, may be employed as fuels.

222 Pure tetranitromethane is a substance that presents virtually no danger. However, in working with it, it is necessary rigidly to observe precautions, and completely to eliminate the possibility of contamination of tetranitromethane by organic substances of any kind.

Production of tetranitromethane. The literature describes more ten methods of producing tetranitromethane, but only a few of these deserve attention from the view point of recommendation for industrial purposes.

1. The acetic anhydride method. Acetic anhydride reacts with strong nitric acid at 25 - 30°, in accordance with the following equation:

$$4(CH_3CO)_2O + 4HNO_3 \rightarrow C(NO_2)_4 + 7CH_3COOH + CO_2.$$

The initial substances are mixed in stoichiometric ratio, and are allowed to stand from 5 - 7 days. The temperature of the reaction mixture has to be 25 - 28°. After standing for 5 - 7 days, the tetranitromethane liberated in the form of a heavy oil on the bottom of the vessel. It is decanted steam-distilled. Tetranitromethane is purified by repeated steam distillation, and is dessicated with calcium chloride. The product yield is 70 - 75% of the theoretical.

The raw materials consumed per ton of finished product are: 1.8 ton HNO_3 (monohydrate) and 3 tons $(CH_3CO)_2O$. The acetic anhydride may be recovered, in which case the absolute consumption of acetic anhydride is about 0.6 ton.

A shortcoming of the acetic anhydride method is the duration of the process.

2. Destructive nitration. When dinitrobenzene or other mono- and dinitro derivatives of the aromatic hydrocarbons are nitrated under severe conditions (high-temperature, strong mixed acid), the reaction proceeds in two directions:

$$C_6H_4(NO_2)_2 \xrightarrow{HNO_3} C_6H_3(NO_2)_3 + H_2O;$$

$$C_6H_4(NO_2)_2 \xrightarrow{+12HNO_3} 3C(NO_2)_4 + 3CO_2 + 8H_2O + 2NO.$$

222 As a consequence of the low yields of both products, the method is not economical. Moreover, the process is very dangerous at high temperature.

3. Nitration of acetylene (Bibl.45, 46). The action of acetylene with strong nitric acid proceeds through several stages and may be described by the following summary equation:

$$5C_2H_2 + 38HNO_3 \rightarrow 3C(NO_2)_4 + 24H_2O + 7CO_2 + 26NO_2.$$

Thus, approximately 60% of the acetylene is converted into tetranitromethane, and the remainder is oxidized. The process apparently may be expressed by the following mechanism:

$$CH{\equiv}CH + HNO_3 \rightarrow (NO_2)CH{=}CH(OH)$$ oxinitroethylene;

$$(NO_2)CH{=}CH(OH) + HNO_3 \rightarrow (NO_2)_2CH - CH(OH)_2$$ dioxidinitroethane;

$$(NO_2)_2CH - CH(OH)_2 \rightarrow H_2O + (NO_2)_2CH - C\begin{matrix}O\\H\end{matrix}$$ dinitroacetic aldehyde;

223

$$(NO_2)_2CH - C\begin{matrix}O\\H\end{matrix} + HNO_3 \rightarrow \ldots$$

$$\ldots HNO_2 + (NO_2)_2CH - C\begin{matrix}O\\OH\end{matrix}$$ dinitroacetic acid;

$$(NO_2)_2CH - C\begin{matrix}O\\OH\end{matrix} \rightarrow CO_2 + (NO_2)_2CH_2$$ dinitromethane;

$$(NO_2)_2CH_2 + HNO_3 \rightarrow H_2O + CH(NO_2)_3$$ nitroform;

$$CH(NO_2)_3 + HNO_3 \rightarrow H_2O + C(NO_2)_4$$ tetranitromethane.

The last of these reactions occurs in the presence of sulfuric acid. Nitroform is produced as an intermediate, and may be isolated by nitrogen dioxide extraction at 0° (Bibl.38).

The possibility of converting acetylene to trinitro- and then to tetranitromethane by nitric acid reaction was discovered in 1900. However, the product yield was 20 - 25%. In 1920, mercury nitrate came to be used as promoter, and the yield was

223 increased to 40 - 45%. Subsequently, it was found that nitrogen oxides have a positive effect upon the yield, and particularly upon the process rate. It was also found that certain metals (Fe, Ni, Co, Al) are inhibitors of this process. Consideration of these factors made it possible to increase the yield of tetranitromethane to 90%.

4. Nitration of Ketene (Bibl.47). Tetranitromethane is obtained by slowly admitting ketene (produced by pyrolysis of acetone) into cooled strong nitric acid. At the conclusion of the reaction, the mixture is poured over ice, and the tetranitromethane which settles out is separated. The yield is 90%. The reaction follows this equation

$$4CH_2=CO+4HNO_3 = C(NO_2)_4+CO_2+3CH_3COOH.$$

PART II

NITROAMINES

CHAPTER VII

GENERAL DESCRIPTION OF NITROAMINES

The polynitro derivatives of the amines are widely employed as high explosives. This class includes RDX and TNT, which are brisant explosives widely employed in the manufacture of detonators and caps, as well as in the filling of munitions.

The iritial materials for the production of nitro amines are the amines of the aromatic, heterocyclic, and aliphatic series, nitric, sulfuric, and, in a number of instances, also acetic acid and acetic anhydride. The production of these explosives is more dangerous than that of the nitro compounds in view of their high sensitivity to temperature and mechanical influences, as well as their high tendency to detonate.

The polynitro amines are usually obtained by nitration of the corresponding amines, in which the nitro group may replace either hydrogen at the carbon ($\equiv CH \xrightarrow[-H_2O]{+HNO_3} \equiv C - NO_2$), or the hydrogen at the nitrogen ($=NH \xrightarrow[-H_2O]{+HNO_3} =N - NO_2$). In the first case, the result is a C-nitro compound and in the latter a N-nitroamine.

The formation of nitro compounds under the effects of nitric acid or mixed acid (so-called C-nitration) proceeds in accordance with the mechanism previously described. The nitrating agent in N-nitration, when strong nitric acid or mixed acid is reacted with an amino compound will also be the nitronium cation $NO_2^{\oplus}$ (Bibl.62), and the reaction will also go in two stages: addition of $NO_2^{\oplus}$ and subsequent detachment of the replaced hydrogen by the proton acceptor (Bibl.3). However, in performing this reaction,

224 it is necessary to take into consideration the presence (of a) readily oxidized amino group in the compound. Therefore, in order to prevent or at least to reduce oxidizing processes, the amino group is stabilized or as they say protected either by obtaining a salt (usually by means of sulfuric acid) or an acyl derivative (by means of acetic acid). The product obtained is then nitrated.

In N-nitration, reactivity is higher than in C-nitration of the unsubstituted benzene. Thus, for example, the unshared electrons of the nitrogen atom in trinitrophenyl-N-methylamine are taken up by the the nitronium cation 1.5 times faster than the unsaturated π-electrons in benzene, but at only 1/17 the rate observed in toluene (Bibl.3).

According to Lang (Bibl.4), N-nitration caused by weak nitric acid occurs in the presence of nitric oxides via the formation of the nitro derivative (by the effect of
225 the nitrosyl-cation $NO^{\oplus}$), which is also analogous to the mechanism of C-nitration.

In choosing a solvent for nitration, it is necessary to bear in mind the possibility that it may change the guiding effect of the amino group. In sulfates, the amino or alkyl amino group direct the nitro group partly to the meta-position (Bibl.5), while acylated alkyl amino groups are directed solely to the ortho- and in some degree to the para-position.

The direction of the nitro group entering the ring is determined in a number of cases by the concentration of sulfuric acid in the nitrating mixture. Thus, if in the nitration of acetanilide the nitrating mixtures include not 100% but 78.8% sulfuric acid, the yield of para-nitroaniline will drop to 23.6%, with a corresponding rise in the yield of the ortho-isomer. This is of practical significance, if we bear in mind that the nitration process always is accompanied by the formation of water diluting the

225 nitrating mixture.

In nitrating various aniline derivatives, it was observed that the formation of the N-nitroamine facilitates the presence in the ring of a nitro group in meta-position with respect to the amino group.

In some cases, N-nitration goes through the stage of salt formation. Thus, in reacting dilute nitric acid with the amine, the consequence is a nitrate salt, because of the fact that the amines are of weak basicity. Subsequent treatment of the salt thus obtained with strong nitric acid or acetic anhydride (Ribl.[4]) results in the production of N-nitroamine. It would appear that this stage involves a stage of dehydration of the salt, accompanied by formation of N-nitroamine, for example, in accordance with the reaction:

$$Ar-NH_2 \cdot HNO_3 \rightarrow Ar\cdot NH-NO_2 + H_2O.$$

Some N-nitroamines, such as nitroguanidine, ~~XXXX~~ or nitro urea are produced specifically via the nitrate salt as intermediate, dehydration of the salt being performed by sulfuric acid.

The reaction follows these mechanisms:

for primary amines

$$RNH_2 + HNO_3 \rightarrow \overset{\oplus}{RNH_3}\overset{\ominus}{NO_3} \xrightarrow{-H_2O} RNH\cdot NO_2;$$

for secondary amines

$$\begin{matrix} R_1 \\ R \end{matrix}\!\!>\!NH + HNO_3 \rightarrow \begin{matrix} R_1 \\ R \end{matrix}\!\!>\!\overset{\oplus}{N}H_2\overset{\ominus}{NO_3} \xrightarrow{-H_2O} \begin{matrix} R_1 \\ R \end{matrix}\!\!>\!N\cdot NO_2.$$

Secondary and tertiary aromatic amines, such as methylaniline, ~~XXXX~~ ethylaniline, or diethylaniline are converted, by the vigorous effect of fuming nitric acid, to monoalkyl-N-nitroamines, and, where the tertiary amines are concerned, cleavage of one alkyl group occurs. Simultaneous with this, nitration of the aromatic ring

225 occurs (Bibl.7):

$$C_6H_5-NH-CH_3 \xrightarrow[-H_2O]{+HNO_3} C_6H_2(NO_2)_3N\begin{matrix}CH_3\\NO_2\end{matrix}.$$

The entry of the nitro group into the ring of an aromatic amine, i.e., formation of the nitro compound, occurs as a consequence of two reactions: regrouping of phenylnitroamine (which is promoted by acid) and nitration by nitric acid. A.I.Titov (Bibl.9), and Hughes and Ingold (Bibl.10) hold that this regrouping is intramolecular in nature and proceeds through intermediate formation of cation by attachment of a proton to the amine nitrogen. This last explains the need to have an acid medium in order for this reaction to go. Subsequently, Hughes and others, employing labeled nitrogen, obtained direct proof of the intramolecular nature of the regrouping (Bibl.10).

Weakly basic amines nitrate readily, whereas strongly basic amines nitrate only in the presence of a promoter (chlorides are usually employed).

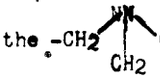
The amine nitration reaction is not infrequently accompanied by a breaking of the C-N bond, the consequence of which another organic molecule, most frequently alcohol, which is then etherified, is formed simultaneous with the N-nitroamine. Nitration with breaking of the C-N bond is called nitrolysis and may be depicted by the following mechanisms:

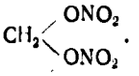
a) nitrolysis with alcohol formation

$$R_2NCH_2R' + HONO_2 \rightarrow R_2N-NO_2 + HO-CH_2R'$$
$$NO_2-O-CH_2R';$$

226 b) nitrolysis with formation of a free alkyl cation (forming a nitrate ester under the influence of the $NO_3^{\ominus}$ ion)

$$R_2NCH_2R' + NO_2^{\oplus} \rightarrow \begin{matrix}R\\R\end{matrix}\!\!>\!\overset{\oplus}{N}\!-\!CH_2R' \rightarrow R_2N\cdot NO_2 + \overset{\oplus}{C}H_2R$$
$$\downarrow +NO_3^{\ominus}$$
$$NO_2-O-CH_2R.$$

226 The reaction by which RDX is formed via nitration of urotropine, which detaches the  -grouping, is a nitrolysis reaction. In addition to RDX, an alcohol nitrate ester is formed, specifically, methyleneglycoldinitrate



A considerable amount of nitrating agent is consumed in producing N-nitroamines, and the reaction is usually run at low temperature, because of the low stability of the side product. These process conditions result in a considerable consumption of materials (raw material, cooling agent) when they are performed on a factory scale, and lead to a high product cost.

On the industrial scale, the production of certain N-nitroamines, specifically cyclotrimethylenetrinitroamine (hexogen) is conducted both by direct nitration of amines and by an indirect method: condensation of formaldehyde with ammonium nitrate in the presence of a promoter (PF_3). In some cases, this is economically more desirable than direct nitration of the amine.

A.Lamberton (Pill.11) holds that N-nitroamines may be regarded as amides of ntric acid. If one hydrogen atom in the simplest inorganic N-nitroamine NH_2NO_2 be replaced by alkyl or aryl groups, the result is the primary N-nitroamine $ArNH \cdot NO_2$. If both hydrogen atoms are replaced, the result is the secondary N-nitroamine $Ar_2N \cdot NO_2$.

The nitroamides (primary and secondary) may be included among the N-nitroamines. The difference between the two lies in the fact that in the latter, one group (Ar) is acid (for example, acyl, sulfanyl, etc.).

The behavior of the C-nitroamines and their properties are analogous to the

226 properties of the nitro compounds, inasmuch as the nitro group therein is directly attached to the carbon atom.

The behavior and properties of the N-nitroamines differ sharply from the properties of the nitro compounds, as the nitro group therein is attached to the nitrogen atom. This bond of the nitro group is weaker than a direct bond to carbon. This is the reason, as a rule, for the fact that the N-nitroamines are less stable than the nitro compounds. The N-nitroamines are usually more sensitive to mechanical effects, and therefore many explosives of this class are employed to fill shells, only in the phlegmatized form.

Characteristic reactions for the N-nitroamines are reduction by hydrogen and the effect of sulfuric acid. When primary N-nitroamines are reduced, hydrazine derivatives result, whereas the reduction of secondary N-nitroamines results in the formation of alkylhydrazine. Vigorous reduction of alkylhydrazines results in reduction of alkylamine and ammonia.

When strong sulfuric acid is reacted with N-nitroamines, the nitro group attached to the nitrogen cleaves away. The primary N-nitroamines are particularly readily subject to decomposition. Under the influence of dilute sulfuric acid, alcohol and N_2O are formed:

$$RNH \cdot NO_2 \rightarrow ROH + N_2O.$$

227 The secondary N-nitroamine are more stable to sulfuric acid and decomposition frequently sets in only at high temperature.

Strong sulfuric acid induces cleavage of the N-nitroamines of the aliphatic or heterocyclic series, accompanied by vigorous liberation of nitrous oxide. In some cases, this reaction leads to the formation of N-nitrosoamines. This behavior of

227 N-nitroamines frequently renders it impossible to obtain them in sulfuric acid as medium.

There also exists a group of isomeric compounds with primary N-nitroamines, which also yield hydroxylamine derivatives on reduction. These compounds differ from the N-nitroamines in that the oxygen atoms are separated:

$$R-\underset{\underset{NO}{|}}{N}-OH$$

which is due to the manner in whi they are obtained, to wit: nitrosification, and not nitration, as is the case of N-nitroamines.

The physical properties of the primary N-nitroamines are completely different than those of the nitroso derivatives of the hydroxylamines. For example, phenyl-N-nitroamines $C_6H_5NHNO_2$ differs substantially from phenyl-N-nitrosohydroxylamine. $C_6H_5\underset{\underset{NO}{|}}{N}OH$. The nitroso hydroxylamines have not yet been studied in terms of their explosive properties.

The structure of N-nitroamines, based on their chemical properties is confirmed by x-ray analysis of the simple N-nitroamines, which show that the atoms of the XXX $N-N\begin{matrix}\nearrow O\\ \searrow O\end{matrix}$ group are in a single plane (Pibl.12).

N-Nitroamines do not display basic properties, whereas the primary ones even have weak acid properties and are capable of yielding salts along with the bases. The acid properties of the primary N-nitroamines are only one twentieth XXXXXXXXX as strong as those of formic acid. Contrariwise, nitroamides are capable of being strong acids, substantially more powerful than formic acid.(this is true for example of nitrourethane).

The primary XX N-nitroamines react readily with ammonia in a benzene medium, yielding ammonia salts. The majority of the N-nitroamines are subjected to denitration when heated with phenol, particularly in the presence of sulfuric acid.

227 Some of the aromatic N-nitroamines, for example, trinitrophenylmethyl-N-nitroamine (tetryl), form addition products with the simplest amines. These addition products are, for the most part, intensively colored. In many cases, these compounds convert to picramide (2,4,6-trinitroaniline) or to its N-alkyl derivatives (Bibl.13).

CHAPTER VIII

THE CHEMISTRY AND TECHNOLOGY OF THE NITROAMINES

A. Tetryl and Other Nitro Derivatives of the Aromatic Amines

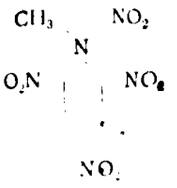
Tetryl was first obtained by Martens in 1877 by heating dimethylaniline with fuming nitric acid. Sometime later Romburgh (Bibl.1) determined the structure of tetryl, and obtained it by nitration of monomethyl- and dimethylaniline. From the fact that nitration of dimethylaniline reveals the formation of CO_2 and abundant liberation of nitrogen oxides, which is hardly to be noticed in the nitration of monomethylaniline, he drew the conclusion that tetryl contains only one methyl group. He found it possible to reinforce this point of view by obtaining tetryl from N-methyl- and N-dimethylpicramide, as well as from picryl chloride and potassium methylnitroamine. Romburgh ascribed the following formula to tetryl: $C_6H_2(NO_2)_3N\begin{matrix}CH_3\\NO_2\end{matrix}$, and it is still accepted today.

22. The explosive properties of tetryl were studied in 1885 - 1886 in the Prussian Department of War by Lenz, who found that tetryl was unsuited to filling shells because of its high sensitivity to friction.

Tetryl has a good sensitivity to detonation, and therefore, starting in 1906, it came into use in detonators and detonating caps. Today, tetryl is of secondary importance, and its production and consumption are being reduced.

Section 1. The Chemistry of Production, the Properties, and the Applications of Tetryl

Tetryl (trinitrophenylmethyl-N-nitroamine) may be obtained from dimethylaniline, monomethylaniline, and benzene (via dinitrochlorobenzene). Its structural formula is

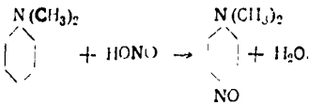


a) Production of Tetryl from Dimethylaniline

On the industrial scale, dimethylaniline is produced by passing aniline bases with methylether (a methanol-production waste) over active aluminum oxide at 230 - 295°. Contact alkylation of aniline by dimethylether makes it possible to produce dimethylaniline which is virtually free of aniline and monomethylaniline as impurities (Bibl.2,3,4,5).

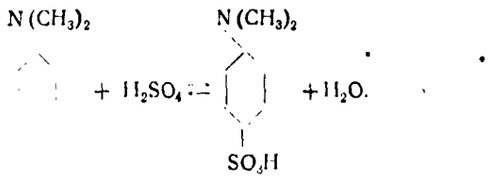
Dimethylaniline is colorless liquid boiling at 193.5°, having a freezing point of +1.96°, and a specific gravity of 0.955. The technical product is from yellow to brown in color.

The highly reactive amino- or alkylated amino group greatly increases the ability of the benzene ring to undergo oxidation and resinification. The para-position relative to dimethylamine group is the most reactive in dimethylaniline. Thus, when nitrous acid is reacted with dimethylaniline, green para-nitrosodimethylaniline is formed:



Dimethylaniline, as a ternary aliphatic-aromatic amine, reacts in one of two ways with concentrated sulfuric acid: it either forms a salt - dimethylanilinesulfate, or dimethylanilinesulfonic acid. The temperature determines the direction in which the reaction goes. At low temperature, (the salt is formed, and at) high temperature (of the order

228 of 180 - 190°), para-sulfonic acid is formed:



229 Dimethylaniline-para-sulfonic acid is a colorless crystalline mass which fuses [illegible] (acquiring a dark shade) at 257°.

At low temperature (40°), dimethylaniline forms a [illegible] salt with sulfuric acid:

$$C_6H_5N(CH_3)_2 + H_2SO_4 \rightarrow [C_6H_5N(CH_3)_2H]\cdot HSO_4,$$

which, at high temperature (over 100°) is capable of undergoing conversion to dimethylaniline sulfonic acid in accordance with [illegible]

$$[C_6H_5N(CH_3)_2H]\cdot HSO_4 \rightarrow C_6H_4(SO_3H)\cdot N(CH_3)_2 + H_2O.$$

The sulfate salt dimethylaniline is a colorless crystalline material having a melting point of 91.5°. It is very hygroscopic, dissolves readily in sulfuric acid, water, and alcohol. Bases cause it to decompose, with liberation of free dimethylaniline. As the salt of a weak base and a strong acid, it hydrolizes readily, to yield an acid reaction.

When dimethylaniline is nitrated with weak [illegible] nitric acid (50%) or mixed sulfuric and nitric acids, at low temperature (0°), mononitrodimethylaniline is obtained

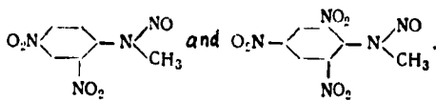
$$C_6H_5N(CH_3)_2 + HNO_3 \rightarrow C_6H_4(NO_2)N(CH_3)_2 + H_2O$$

as is dinitrodimethylaniline

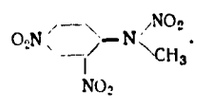
$$C_6H_3(NO_2)_2N(CH_3)_2.$$

According to Orton (Bibl.6), the presence of nitrous acid is required to nitrate dialkylanilines. In his opinion, an intermediate may come into being here - the nitroso compound ON · C_6H_4 · $N(CH_3)_2$, which is subsequently oxidized to the nitro [illegible]

229 compound. A study by Lang (Bibl.7) gives some support to this view. Lang reacted nitric acid with dimethylaniline to produce a mixture of di- and trinitrophenylmethyl-N-nitrosoamines:



Stronger nitric acid results in the formation of dinitrophenylmethyl-N-nitroamine



Later, (Bibl.8,9) it was determined that the reaction of conversion of dinitrodimethylaniline to tetryl is promoted by nitrogen oxides (nitrous acid) which, at the same time, constitute a powerful demethylating agent.

Hodgson (Bibl.10) and Urbanskiy (Bibl.11) having studied the effect of nitric acid of various concentrations upon dimethylaniline, found that at 0°, reaction of 99.6% nitric acid results in the formation of N-nitro-2,4,6-trinitromethylaniline; 70% nitric acid yields 2,4,6-trinitromethylaniline; 54% and 40% nitric acid yields 2,4-dinitrodimethylaniline, and reaction of 20% nitric acid yields a mixture containing about 40% 3,3',5,5'-tetranitro-N,N,N',N'-tetramethylbenzidine and about 60% 2,4-dinitrodimethylaniline. The reaction does not occur if the nitric acid is weaker. With increase in temperature, cleavage of the methyl group is observed, as is the case when 50% and 40% nitric acids are used. With 20% nitric acid, it is only nitration that occurs.

Sodium nitrite accelerates the reaction, and urea has the opposite effect.

229 Comparative tests show (Bibl.8), that nitrous acid is a more effective demethylating agent than is nitric acid.

230 The sequence of nitration of dimethylaniline by nitric acid may be represented by the following mechanism (Bibl.8,10):

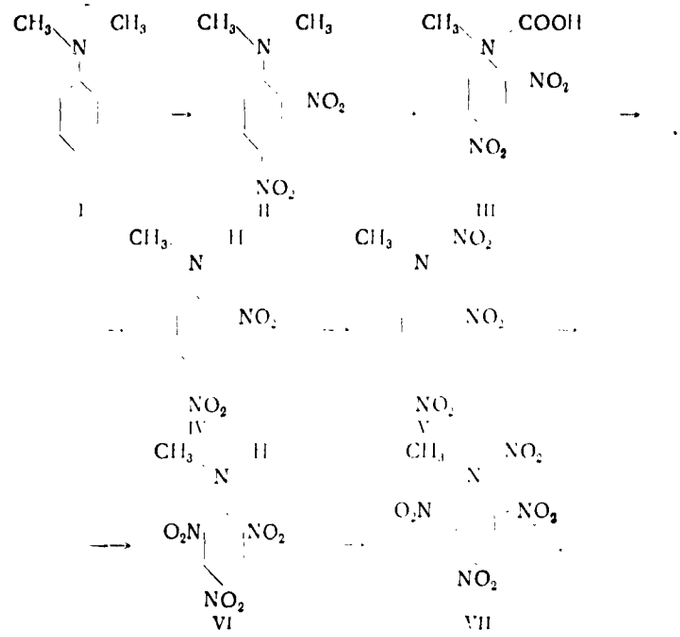


Table 76 presents the properties of the nitro derivatives of dimethylaniline.

Table 76

Compound	Melting Point, °C	Appearance
Para-nitrodimethylaniline	161 - 162	Yellow crystals with steely cast
Ortho-nitrodimethylaniline	20	Free-flowing orange oil
Meta-nitrodimethylaniline	60 - 61	Red crystals
2,4-Dinitrodimethylaniline	87	Bright yellow crystals
2,6-Dinitrodimethylaniline	78	-
3,4-Dinitrodimethylaniline	174 - 175	-
3,5-Dinitrodimethylaniline	112	-

When dimethylaniline is nitrated in two stages (Bibl.10), first by weak, and then by strong nitric acid or mixed acid, the tetryl is obtained by the following

230 probable [illegible] mechanism:

first stage

$$C_6H_5N\begin{matrix}CH_3\\CH_3\end{matrix} + 2HNO_3 \rightarrow C_6H_3(NO_2)_2N(CH_3)_2 + 2H_2O;$$

second stage

$$C_6H_3(NO_2)_2N(CH_3)_2 + 8HNO_3 \rightarrow$$
$$\rightarrow C_6H_2(NO_2)_3N(CH_3)(NO_2) + CO_2 + 6NO_2 + 6H_2O.$$

231 On the industrial scale, this method is not employed, due to the large consumption of acids (ratio of mixed acid to dimethylaniline 50:1). A smaller consumption of concentrated acid occurs when the process is run in such fashion as to cause oxidation of the methyl group in accordance with the equation

$$C_6H_5N(CH_3)_2 + 8HNO_3 \rightarrow C_6H_3(NO_2)_2NH(CH_3) + 6H_2O + 6NO_2 + CO_2,$$

and in the second phase, there is further nitration:

$$C_6H_3(NO_2)_2NH(CH_3) + 2HNO_3 \rightarrow C_6H_2(NO_2)_3NCH_3(NO_2) + 2H_2O.$$

However, this variant of the process is also quite complex in the [illegible] technological sense. [illegible]

In industry, tetryl is obtained from dimethylaniline in two stages. In the first stage, dimethylaniline is converted to the sulfate salt by treatment with commercial sulfuric acid. In the second stage, the dimethylaniline sulfate obtained is nitrated with concentrated nitric acid or melange. Running the process in this way is most practicable, inasmuch as the activating effect of the amino group, causing the oxidizing processes, is diminished by conversion to the more stable sulfate salt. This may be seen from the following example: dimethylaniline added to the melange (at 20 - 40°) immediately flashes with formation of an oily black substance, while [illegible] dimethylanilinesulfate nitrates to tetryl under these conditions.

231 Theoretically, production of dimethylanilinesulfate requires 0.81 part H_2SO_4 by weight per part dimethylaniline. However, in practice, 8 parts sulfuric acid is employed by weight, in the form of 93 - 94% commercial sulfuric acid. The large excess of sulfuric acid makes for complete conversion of the dimethylaniline to salt, and its solution in excess acid. The excess acid goes to strengthen the mixed acid. Reduction in the amount or concentration of the sulfuric acid may lead, on the one hand, to incomplete neutralization, which in turn results in flash when the salt is run into melange, while on the other hand it results in producing weak mixed acid, inducing premature oxidation, foaming of the nitro mass, and reduction of the quality of the tetryl.

The process of neutralization runs at 35 - 40°. Increase in temperature may induce partial resinification of the dimethylaniline, as well as the formation of sulfonic acid, nitration of which yields unstable side products and reduces the tetryl yield.

Production of the sulfate salt dimethylaniline is a very critical operation, and the skill with which it is performed governs the yield of tetryl, as well as the safety of the process, to a considerable degree.

The conversion of dimethylaniline to the salt IX may be checked by the appearance of the reaction liquid: transluscence and the lack of oily spots on the surface when diluted with water is a reliable proof of the absence of free dimethylaniline.

Dimethylanilinesulfate may be nitrated either by concentrated nitric acid or by melange. Nitration with melange goes more quietly, as the nitrogen oxides are in the form of nitrosyl sulfuric acid. However, upon nitration with nitric acid, the nitrogen oxides contained therein give rise to resinification of dimethylanilinesulfate.

231 When tetryl is formed from dimethylanilinesulfate, two reactions occur: nitration and oxidation. One of the methyl groups is subjected to oxidation, and a nitro group has to take its place. Oxidation of the methyl group goes thanks to the nitric acid, which is reduced to NO_2 and NO. Depending upon the degree of reduction of the

232 nitric acid, the consumption will vary and the reaction will be expressed by one of two equations:

$$C_6H_5N(CH_3)_2 \cdot H_2SO_4 + 10HNO_3 \rightarrow$$
$$\rightarrow C_6H_2(NO_2)_3N\begin{matrix}CH_3\\NO_2\end{matrix} + H_2SO_4 + 6NO_2 + CO_2 + 8H_2O. \qquad (I)$$

$$C_6H_5N(CH_3)_2 \cdot H_2SO_4 + 6HNO_3 \rightarrow$$
$$\rightarrow C_6H_2(NO_2)_3N\begin{matrix}CH_3\\NO_2\end{matrix} + H_2SO_4 + 2NO + CO_2 + 6H_2O. \qquad (II)$$

When the reaction follows the first equation, 5.2 parts nitric acid monohydrate are required per part by weight of dimethylaniline. In practice, it is this ratio that is employed. However, the residue of nitric acid remaining in the spent acid (as much as 8%) indicates that the reaction goes, in part, in accordance with the second equation.

In nitration of dimethylanilinesulfate, the nitro groups obviously enter the ring at the outset. Upon entry of electrically negative NO_2 groups into the benzene ring, the major properties of dimethylaniline disappear, the existence of the sulfate salt becomes impossible, and the attached sulfuric acid detaches. At this time, the mixed acid is diluted somewhat with reaction water, and its oxidizing effect increases. Subsequently, oxidation of one methyl group to carboxyl, with subsequent detachment of CO_2, sets in.

Despite the fact that the activating effect of the displaced amino group is

232 substantially diminished by the attachment of sulfuric acid in dimethylanilinesulfate, this salt nevertheless oxidizes and resinifies rather easily, and therefore nitration has to be conducted with great care. Nitration is performed by running in a sulfate solution of dimethylaniline salt to melange in the nitrator. If the reverse procedure were used in run-in, powerful oxidizing processes would occur, and ignition of the product might occur.

Nitration is performed in a specific temperature interval (50 - 60°) and deviation from this results in pronounced change in the process. Reduction in the temperature of onset of nitration inhibits oxidation of the methyl group and therefore, even an increase in the time does not make it possible to obtain a high yield and good-quality tetryl. Moreover, at low temperature, in view of the negligible reaction velocity, unreacted product accumulates in the apparatus, and this presents a great danger. Nitration at higher temperature results in deeper oxidation than is required for the production of tetryl, and therefore results in a reduction in yield and impairment of the quality of the latter. Tetryl produced at high temperature is darker in color, due to the partial resinification.

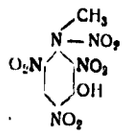
The temperature of 150°, at which flash of the reaction mass occurs, is critical. From the point of view of safety, nitration is best performed at 60°. Under these conditions, most of the component mixture is able to react during run-in, and if cessation of stirring or cooling occurs, the heating of the mass due to continued reaction will be small.

The unpurified tetryl obtained from dimethylaniline contains a small quantity of impurities, which reduce its freezing point by 1.5 - 2°.

The major impurity is tetranitrophenylmethyl-N-nitroamine (meta-nitrotetryl), in

232 which the nitro group in the meta-position is readily replaced by hydroxyl when boiled with water, and forms trinitromethyl-N-nitroaminophenol

233

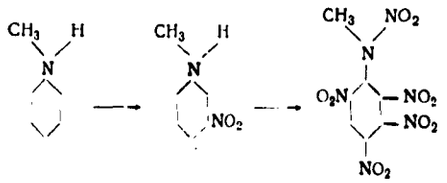


Thanks to the presence of three nitro groups in the ring, the hydrogen atom of the hydroxyl has a pronounced acid nature, in connection with which trinitromethyl-N-nitroaminophenol has the properties of a strong organic acid and communicates residual acidity to tetryl.

Trinitromethyl-N-nitroaminophenol reacts freely with alkalis, carbonates, and metal oxides, to form phenolates.

An increase in the yield of metanitrotetryl is facilitated by the use of low-grade dimethylaniline, containing up to 0.3% monomethylaniline, as well as by the use of mixed acid of increased strength or by increasing the quantity of sulfuric acid therein, inasmuch as, under these conditions, there is an increase in the meta-orienting effect of the $N(CH_3)_2 \cdot H_2SO_4$ group.

According to Romburgh (Bibl.12), the formation of meta-nitrotetryl proceeds through the formation of mononitromethylaniline:



An increase in the temperature of nitration also makes for an increase in the yield of meta-nitrotetryl.

Meta-nitrotetryl diminishes the stability of tetryl. With a 1% meta-nitrotetryl content, the time required for an Abel specimen diminishes to 15 min (instead of

233 25 min), and when the content is 10%, it is reduced to three minutes. According to Obermueller, meta-nitrotetryl yields an increase in pressure of 588 mm per hr, while purified tetryl causes a rise of only 20 - 30 mm. Thus, meta-nitrotetryl decomposes 25 times more rapidly than does tetryl.

Meta-nitrotetryl also is responsible for the acidity of tetryl, inasmuch as, when reacted with water, it hydrolizes to nitrous acid and trinitromethyl-N-nitroaminophenol. Meta-nitrotetryl also affects the color of tetryl to a considerable degree, giving it a bright greenish tint under certain circumstances.

The yield of meta-nitrotetryl may be reduced by employing quality dimethylaniline, not containing monomethylaniline, and by the use of a less concentrated mixed acid. However, this results in turn, in increasing the contents of incomplete nitration products in the tetryl, which results in a reduction in the quality and the yield of the basic product.

b) Production of Tetryl from Monomethylaniline

Monomethylaniline is obtained by passing an alcohol solution of aniline, containing PCl_3 through a system of autoclaves (Bibl.13), or by reacting an aqueous methylamine solution upon chlorobenzene in the presence of combined copper (Bibl.14).

Monomethylaniline is a transparent liquid ranging from yellow to brown in color, boiling at 195.5°. Its freezing point is -57°, and its specific gravity is $d_{4^\circ}^{20^\circ} = 0.989$. The chemical properties of monomethylaniline are very similar to those of dimethylaniline. However, monomethylaniline is somewhat more reactive than dimethylaniline. This is expressed, in part, by the fact that it oxidizes more readily and resinifies upon reaction with nitric acid.

Martens, nitrating monomethylaniline with weak nitric acid (10 parts 50% HNO_3 by

233 weight per part monomethylaniline) obtained trinitromonomethylaniline.

234 Desvergnes (Bibl.15) developed a two-stage method of nitration of monomethylaniline to tetryl. The following reactions occur therein:

$$C_6H_5NHCH_3 + 2HNO_3 \rightarrow C_6H_3(NO_2)_2NHCH_3 + 2H_2O;$$
$$C_6H_3(NO_2)_2NHCH_3 + 2HNO_3 \rightarrow C_6H_2(NO_2)_3N(NO_2)CH_3 + 2H_2O.$$

As is evident from the equations adduced, it is not necessary, in nitrating monomethylaniline, to expend nitric acid upon the oxidation of the methyl group, and therefore, the consumption thereof has to be considerably less than in the nitration of dimethylaniline. This makes for what is indubitably an expedient process. However, this process has not come into practical use, apparently because of the complexity of work with dilute nitric acid. However, the nitration of monomethylaniline through the sulfate salt stage, as occurs when tetryl is made from dimethylaniline may result in the production of a considerable amount of meta-nitrotetryl.

Table 77 presents some of the properties of the nitro derivatives of monomethylaniline.

Table 77

Compound	Melting point, °C	Appearance
Para-nitromonomethylaniline	150 - 151	Yellow-brown crystals with violet shading
Ortho-nitromonomethylaniline	34 - 35	Red crystals with violet shading
Meta-nitromonomethylaniline	65 - 66	Reddish-yellow crystals
2,4-Dinitromonomethylaniline	176.7	Canary yellow crystals
2,6-Dinitromonomethylaniline	106	-
2,5-Dinitromonomethylaniline	161	-

When monomethylaniline is nitrated to tetryl, the following amounts of heat are liberated (Bibl.16):

methylaniline to para-nitromethylaniline - 36.4 kcal/mole; para-nitromethylaniline

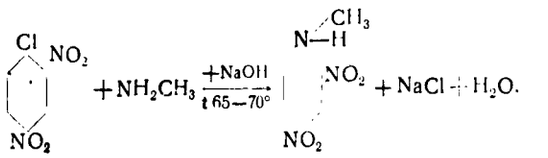
234 to 2,4-dinitromethylaniline - 25.2 kcal/mole; 2,4-dinitromethylaniline to 2,4,6-trinitromethylaniline - 11.9 kcal/mole; 2,4,6-trinitromethylaniline to tetryl - 1.0 kcal/mole.

c) Production of tetryl from chlorobenzene and methylamine. Synthesis of tetryl from chlorobenzene goes through a number of stages:

1) production of dinitrochlorobenzene

$$C_6H_5Cl + 2HNO_3 \rightarrow C_6H_3(NO_2)_2Cl + 2H_2O;$$

2) production of dinitrophenylmethylaniline (melting point 176.7°) (Bibl.17)



The reaction of replacement of chlorine by the alkylamino group is able to be run in organic solvents with copper catalyst (Bibl.18).

Nitration of dinitromonomethylaniline by mixed acid containing 16 - 17% water at 30 - 40° results in a 95% yield of tetryl having a melting point of 128.1- 128.4° (Bibl.19). This method of producing tetryl is less dangerous than production from dimethylaniline. A considerable advantage therein also lies in the fact that dinitrochlorobenzene is simultaneously an intermediate product for production of

235 synthetic dyes. The second starting product - methylamine-is, under standard conditions, a gas, and is usually employed either as a salt (sulfate) or as an aqueous solution (solubility in 100 gm of water at 25° is 959 cm^3, and in ether solubility is virtually unlimited).

The specific gravity of methylamine is $d_{4^\circ}^{70^\circ} = 0.7691$, its melting point is 92.5°, and is boiling point 6.5°.

Methylamine is produced by reacting formaldehyde with ammonium chloride (Bibl.20) or from acetic acid and ammonia.

Properties of tetryl. Tetryl is a white crystalline substance. The technical product is bright yellow. The specific gravity of tetryl is 1.73, and its gravimetric density is 0.9 - 1 gm/cm^3. Tetryl is readily ~~susceptible to passing~~ to a density of 1.60 - 1.63 gm/cm^3 (at P = 2000 kg/cm^3 ~~may be pressed~~ to 1.71).

The melting point of tetryl is 129.45° (fusion is accompanied by decomposition), the freezing point of chemically pure tetryl is 128.5°, and that of technical tetryl 127.7°. The specific heat capacity of tetryl at 20° is 0.218 kcal/gm°C (Bibl.21). Its melting point is 20.6 kcal/gm.

Tetryl is nonhygroscopic, and very slightly soluble in water (0.019% at 50°, and 0.184% at 100°). The solubility of tetryl in various solvents is presented in Table 78.

Tetryl is a neutral substance and does not react with metals, but does react with alkalis and sodium and potassium carbonates. When tetryl is heated with dilute solutions of alkalis, picrates result (Bibl.22):

$$C_6H_2(NO_2)_3N\begin{matrix}CH_3\\NO_2\end{matrix}+2NaOH \rightarrow NaNO_3+CH_3NH_2+C_6H_2(NO_2)_3ONa.$$

When tetryl is heated with water over a long period, it decomposed slowly to form picric acid.

The addition of up to 10% sodium picrate virtually does not change the shock sensitivity of tetryl, but merely reduces its melting point by 0.6°. Therefore, soda has been used in France to accelerate the washing of acids out of tetryl

(Bibl.23).

With alcohol solutions of alcoholates, a toluene solution of tetryl forms metallic derivatives, usually the metallic derivatives of trotyl.

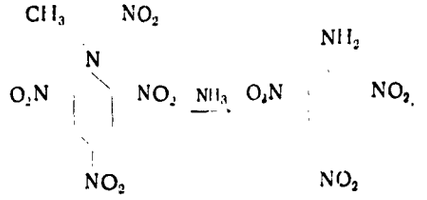
The metallic derivatives of tetryl are carmine red substances having a flash point between 93 - 115°, and similar to mercury fulminate in shock sensitivity

Table 78

a)	b)							
	c)	d)	e)	f)	g)	h)	i	j)
0	0,005	3,45	—	1,5	0,32	0,007	0,188	0,009
17	0,007	—	—	—	0,49	0,020	—	0,017
20	0,008	9,99	45,82	3,8	0,56	0,025	0,418	0,021
30	0,008	—	—	—	0,76	0,039	0,493	0,029
40	0,011	—	—	7,7	1,12	0,058	—	0,056
45	0,014	—	—	—	1,38	0,073	—	0,094
50	0,019	—	111,85	—	1,72	0,095	—	—
60	0,035	—	—	18,8	2,64	0,154	—	—
70	0,053	21,86	—	—	4,23	0,241	—	—
75	0,066	—	—	—	5,33	0,297	—	—
80	0,081	42,43	—	64,5	—	—	—	—
100	0,184	—	—	—	—	—	—	—

a) Temperature, °C; b) Grams of tetryl dissolving in 100 cm³ of;
c) Water; d) Benzene; e) Acetone; f) Dichloroethane; Ether;
g) Alcohol; h) Carbon tetrachloride; i) [illegible] j) Carbon disulfide

236 When gaseous ammonia is admitted in the cold into an alcohol acetone solution of tetryl, the solution becomes dark red. Heating results in the gradual disappearance of the red coloring and the liberation of picramide (Bibl. 24):



In the presence of metallic mercury, sulfuric acid liberates one atom of nitrogen from tetryl in the form of nitrogen oxide. According to the data of A.A.Solonina, the following reactions occur accompanying this:

$$2C_6H_2(NO_2)_3N\begin{matrix}CH_3\\NO_2\end{matrix}+2H_2SO_4=2C_6H_2(NO_2)_3N\begin{matrix}CH_3\\SO_3H\end{matrix}+2HNO_3;$$

$$2HNO_3+6Hg=3Hg_2O+2NO+H_2O;$$

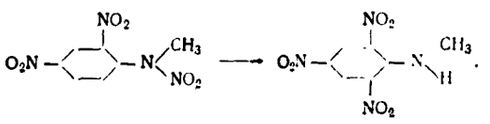
$$3Hg_2O+3H_2SO_4=3Hg_2SO_4+3H_2O;$$

$$2C_6H_2(NO_2)_3N\begin{matrix}CH_3\\NO_2\end{matrix}+5H_2SO_4+6Hg=$$

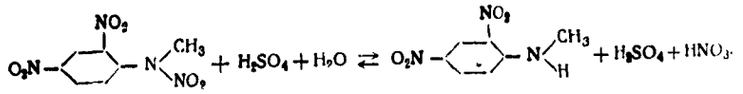
$$=2C_6H_2(NO_2)_3N\begin{matrix}CH_3\\SO_3H\end{matrix}+3Hg_2SO_4+2NO+4H_2O.$$

The reaction of tetryl with sulfuric acid, leading to the formation of trinitrophenylmethyl sulfamine, also occurs in the absence of mercury, but this is apparently a reversible reaction, and the equilibrium is shifted sharply from right to left. However, in the presence of mercury, when HNO_3, which reacts with it, is eliminated from the sphere of [illegible] reaction, the equilibrium shifts from left to right.

We know, that when concentrated sulfuric acid acts upon dinitrophenylmethylnitroamine (in the absence of nitric acid), regrouping occurs, as a consequence of which [illegible] trinitrophenylmethylamine is formed by the following mechanism



The weak (not over [illegible] 70%) sulfuric acid does not cause this [illegible] rearrangement, but merely the expulsion of the nitro group from the side chain, with formation of dinitrophenyl methylamine:



In tetryl, all the ortho- and para-positions in the ring, with respect to the amino group, are occupied, and therefore, not only weak, but concentrated sulfuric acid will result not in rearrangement, but expulsion of the nitro group at the nitrogen.

With 68% trotyl, tetryl forms a eutectic mixture melting at 67 - 68.5° (Bibl.25).

Tetryl is more poisonous than trotyl and particular care must be exercised in working with it (Bibl.26).

237 The stability of tetryl is somewhat lower than that of trotyl and other nitro compounds, but it is nevertheless sufficient for long-term storage under normal conditions.

According to the data of the laboratory of the Okhta Works (Bibl.23), tetryl withstood the Abel test (at 100°) for 20 min after being heated for 2 yrs at 60°. When tetryl was held at 75° for 320 days, the weight loss was 0.3%, but at 110° it attained 11.5% within only 16 days.

The shock sensitivity of tetryl is higher than that of trotyl and nitric acid. Tetryl explodes when a 2-kg weight is dropped from an elevation of 40 cm, and its flash point is 190°. The explosive properties of tetryl may be characterized as follows: temperature of explosion 1100 kcal/kg; volume of gaseous explosion product 765 ltr/kg, work performed in Trauzl block 340 cc, brisance Hess 19 mm, ~~due to Hess,~~ velocity of detonation (at 1.63 density) 7500 m/sec. Tetryl

is more susceptible to detonation than trotyl. The maximum initiating charge of mercury fulminate for pressed tetryl is 0.29 gm, and for lead azide is 0.03 gm.

Tetryl is employed primarily to make detonators, booster charges for combined capsules and detonators, and in detonating fuses, and occasionally as a bursting charge in small-caliber shells, sometimes in the phlegmatized form.

Section 2. Technology of Tetryl Production

a) Production of Tetryl from Dimethylaniline

The technological process for the production of tetryl includes the following stages:

1) Production of dimethylaniline sulfate;

2) Nitration of dimethylaniline sulfate;

3) Processing of the tetryl, consisting of washing and crystallization;

4) Recovery of the mother solvents;

5) Drying of the tetryl.

Figure 65 illustrates the process of tetryl manufacture (Bibl.16).

Production of dimethylaniline sulfate. Dimethylaniline is gradually (over a period of 50 - 60 min) run into a neutralizer (3), at 35 - 45°, into which commercial sulfuric acid has first been run. When run-in is completed, it is held (15 min) at 45 - 50°, and a sample for analysis is taken.

The solution of dimethylaniline sulfate should be a homogeneous transparent liquid, brown in color, and having the specific gravity of 1.68 - 1.70. The total acidity of the solution fluctuates in the range of 83 - 84%. The composition of the solution of the dimethylaniline sulfate is (in %):

H_2SO_4 (monohydrate)	83.0 - 83.8
Dimethylaniline sulfate	10.4 - 10.5
Water	5.8 - 7.1

Nitration of dimethylaniline sulfate. A sulfate solution of dimethylaniline sulfate is added slowly to the nitrator (7), filled with melange and heated to 40 - 45°. The rate of run-in should guarantee that the temperature will rise to 50° in the first 5 min, and to 60° thereafter (1 - 1.5 hrs). The temperature of the nitro mixture is regulated by the rate of run-in and cooling.

Upon conclusion of run-in, the mixture is held for 10 min at 58 - 60°, whereupon the resultant tetryl is monitored in terms of its color (against a control color scale). Tetryl, wetted with water, should be bright ~~XX~~ yellow. If the color product is dark yellow or reddish color this means that the nitration process has not been completed and the mixture must be held for an additional period, with the addition of a little more melange to the nitrator.

At the end of the sulfate run-in period, foam is formed because of the abundant liberation of gaseous ~~XX~~ products of oxidation. During the holding time, formation of foam gradually ceases. If foaming is particularly abundant, the charging of the salt must be stopped and a careful observation of temperature must be maintained, so that it does not rise above the permitted limit. Sometimes, if foaming is strong, it is useful to add a little melange. This reduces the viscosity of the mixture and facilitates removal of gases.

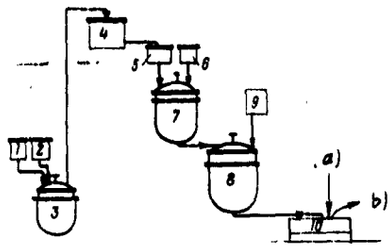


Fig.65 - Diagram of Production of Tetryl from Dimethylaniline (DMA)

1 - Commercial sulfuric acid metering tank; 2 - Dimethylaniline metering tank; 3 - Neutralizer; 4 - Sulfate salt collector; 5 - Sulfate salt metering tank; 6 - Melange metering tank; 7 - nitrator; 8 - Diluter; 9 - Water tank; 10 - Filter and hopper

a) Water; b) Tetryl to washing

At the end of nitration, the nitrator contents are run into diluter (8), half filled with water. Dilution is performed with intensive mixing, and temperature not over 50°.

Treatment of the tetryl. The dilute nitro mass is discharged to the filter-hopper, where the tetryl is separated from the spent acid and washed with cold water. After washing, the tetryl contains 0.5 - 1% residual acid, while the tetryl going to recrystallization should contain, upon recrystallization from benzene, not more than 0.15% acid, whereas upon recrystallization with acetone it contained not more than 0.11% acid. The required acidity may be attained by increasing the number of washings with cold water (to 6 - 7); however, after this, the tetryl has a low freezing point, and it is therefore treated several times in vats of boiling water.

At identical acidity, the freezing point of tetryl will differ very sharply,

depending upon the method of washing. The mean increase in freezing point after boiling is 1.4° (from 126.0 to 127.4°). In the process of washing tetryl with hot water, and boiling, not only are the mineral acids removed, but the organic acid impurities, which reduce the temperature at which tetryl freezes. Tetryl washed only with cold water cannot be recrystallized, as under these conditions the solvent is rapidly saturated with impurities, and partial replacement is required.

In order to accelerate the washing of tetryl, the traces of acids and other impurities in tetryl are removed by cooking in dilute soda solutions, at certain plants in the United States.

In technical tetryl, the following impurities are found after washing with water: dinitromonomethylaniline; tetranitrophenylmethylnitroamine (meta-nitrotetryl); products of the resinification of dimethylaniline, as well as of monomethylaniline, which are always present in technical dimethylaniline; inorganic acids; mineral salts and mechanical impurities carried into the tetryl with the acids and wash water; products of hydrolysis of tetryl and meta-nitrotetryl.

The product of the lower degrees of nitration of dimethylaniline, and the product of resinification reduce the susceptibility of tetryl to detonation, and its brisance. The products of the higher degrees of nitration result in reduced chemical stability of the tetryl. (The uncrystallized tetryl will stand an Abel test for a few minutes, whereas tetryl recrystallized from solvent will stand it for tens of minutes).

The presence of mechanical impurities that have entered as a consequence of

corrosion of the apparatus or inadequate purification of the water entering for washing increases sensitivity to mechanical effects, which also makes for the need for further purification of tetryl by recrystallization.

Of the large number of solvents in which tetryl is soluble to a greater or lesser degree, only acetone, benzene, and nitric acid are of practical value.

Acetone is the best solvent. Tetryl crystallized from acetone has a high solidification point and forms crystals of spicular form, which flow rather freely and are therefore convenient for the filling of detonator caps. Crystallization from benzene yields tetryl having a somewhat lower freezing point. A product is obtained in the form of small crystals and flows poorly, making it difficult to use if for filling. However, this method makes it possible to wash tetryl in solution and is therefore employed in industry (Bibl.16).

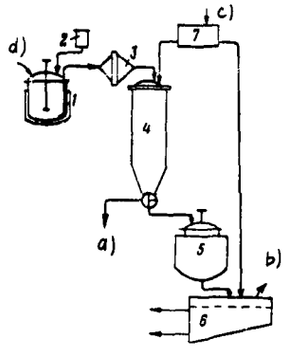


Fig.66 - Diagram of Recrystallization of Tetryl from Benzene

1 - Solvent; 2 - Benzene metering tank; 3 - Filter; 4 - Washing apparatus; 5 - Crystallizer; 6 - Vacuum hopper; 7 - Hot water tank

a) Wash water; b) Tetryl to drying; c) Steam; d) Tetryl

Desvergnes (Bibl.15) has described the purification of tetryl with nitric acid. He has demonstrated the good solubility of tetryl in nitric acid and its suitability for purposes of crystallization of tetryl.

A significant shortcoming of this method is the difficulty involved in the subsequent washing of the tetryl free of nitric acid.

Recrystallization of tetryl from benzene is illustrated in the diagram in Fig.66 (Bibl.16).

The benzene is run into solvent (1) from metering tank (2), and raw tetryl is charged in. At the conclusion of the charging period the contents of the dissolving unit are heated, with stirring, to 65 - 70°, and held until the tetryl has dissolved completely. The solution obtained is forced through filter (3) and washing apparatus (4), to which hot water is added. The washed tetryl solution is lowered into crystallizer (5), which has first been heated to 30 - 35° to avoid the formation of a crust of crystals on the cold parts of the apparatus. After charging and stirring of the solution for 10 min at 65 - 68°, it is cooled, with a slow reduction in temperature to 15 - 20° (in a 3 - 4 hr period).

When crystallization has come to completion, the crystallizer contents are discharged to the vacuum hopper (6), with the agitator working. The tetryl is separated out and washed once or twice with benzene. The mother benzene is used several times. From the vacuum hopper, the tetryl is unloaded into sacks and sent to drying. The tetryl crust formed on the walls of the crystallizer is removed with the mother solvent at 70 - 75°.

240 A special feature of the crystallization of tetryl out of acetone is the impossibility of performing aqueous washing of the solution, as a consequence of which removal of the acid impurities from the solution of tetryl in acetone is ~~[illegible]~~ ruled out. When the mother liquor is used repeatedly, the acidity both of the tetryl and of the solvent increases sharply. As early as the second cycling of the mother acetone, the acidity of the tetryl prior to washing with alcohol (on the vacuum-hopper) exceeds 0.020%. After 12 - 13 cycles of the mother liquor, the acidity of the tetryl rises to 0.090 - 0.100%, and the acidity of the mother acetone ~~achieves~~ reaches 1%. Therefore, the care with which the mother

acetone is separated from the crystallized tetryl is even more important in this situation for the quality of the final product than upon crystallization from benzene. Particularly great is the effect of the residual unremoved mother acetone upon the acidity of the tetryl. Removal of acid impurities from the tetryl was achieved by careful centrifuging of the mother acetone, as well as by the use of crystalline tetryl alcohol for washing.

Crystallization of tetryl out of acetone is performed as follows.

The tetryl is first dried to a moisture content of not more than 0.4% (if moist tetryl is to be crystallized, the quantity of acetone is sharply increased). Pure acetone (or mother acetone with pure acetone added) and tetryl are charged into the solvent. One part tetryl by weight is charged in, per part pure acetone by weight. When mother acetone is employed, 1.4 part mother acetone is charged per part tetryl by weight .

Upon conclusion of the charging, the contents of the dissolving units are heated (with stirring) to 57 - 62°, and held for 20 min, subsequent to which the filter is driven from the solvent into a crystallizer. In the crystallizer, the solution is slowly cooled (over a 3 - 3.5 hr period, with stirring) to 15 - 20°, whereupon the crystallizer contents are delivered to the vacuum-hopper to centrifuge the mother solvent. After careful removal of mother acetone, the crystallized tetryl is washed on a vacuum-hopper with alcohol, centrifuged to separate from the alcohol-acetone mixture, and sent to drying.

The mother solution may be used as many as 13 times in the crystallization process, and is then redistilled after it has become saturated with impurities.

Recovery of mother solvents. After being employed through many cycles, the mother solvents become saturated with impurities, from which they are cleansed by distillation. To do this, the mother benzene is placed in the distillation still, and is heated with spent steam to 55 - 60°. At this temperature, live steam is fed into the still. The water vapors and benzene pass through a rectifier to a condenser, where they are condensed and collected in a receiver. The distilled benzene is returned to the tetryl crystallization cycle. The still residues are cooled, drained to the vacuum-hopper, centrifuged free of water, and sent to be burned. Before distillation of the mother acetone, it is diluted with water through concentration of 40 - 45%. The mass is stirred for 40 min, and then discharged into the vacuum centrifuge.

The centrifuge tetryl is subjected to recrystallization. The filtered, diluted acetone is charged into a still and heated with spent steam. The acetone fumes go through a rectifier and condenser. In the 62 - 70° temperature interval, the first fraction, consisting of acetone at a concentration of more than 92%, is taken off. This acetone is reused as a solvent in the crystallization of tetryl. The second fraction, consisting of 50 - 55% acetone, which is then redistilled, is taken off in the 70 - 90° interval. The still residues are centrifuged free of water and sent to be burned.

241 Drying the tetryl. The drying of crystallized tetryl is performed in rack-type dryers or in vacuum desiccators. Tetryl crystallized out of benzene is dried at 60 - 65° for 24 - 32 hrs, and, if crystallized out of acetone, the temperature is 75° and the time 14 - 18 hrs. Upon completion of drying, tetryl is sent through a No.10 sieve, packed, and made up into lots.

The tetryl has to satisfy the following specifications (Bibl.16):

- Appearance - crystalline powder with no mechanical impurities visible to the eye;

- Color - bright yellow, and homogeneous throughout. For tetryl obtained upon crystallization from benzene, a yellow color is permissible;

- Freezing point, °C - not less than 127.7;

- Temperature and volatile substances in % - not more than 0.02;

- Impurities insoluble in acetone in % - not more than 0.1;

- Total acidity, in terms of H_2SO_4 in % - not more than 0.01.

Types of tetryl rejects: a) rejects due to freezing temperature are corrected by washing on the vacuum-hopper with benzene or acetone, or by recrystallization; b) rejects due to acidity are corrected by washing with hot distilled water on the vacuum-hopper; c) rejects due to color (green tetryl) cannot be corrected, and the product is burned.

b) Production of Tetryl from Chlorobenzene and Methylamine (Bibl.16, 27, 28, 29,30)

The production of tetryl from chlorobenzene and methylamine consists of the following processes: production of dinitrochlorobenzene, production of dinitromonomethylaniline, and production of tetryl. The first two processes were performed, in Germany, where this was the method used in World War II, at plants manufacturing dye intermediates, and the latter process - nitration of dinitromonomethylaniline - was performed at an explosives plant.

The production of dinitrochlorobenzene has been described previously (see p.201). Dinitromonomethylaniline is obtained by condensation of dinitrochlorobenzene with methylamine in aqueous solution.

241 Methylamine may be produced by heating a mixture of ammonium chloride and formalin at 105 - 108° for 2.5 hrs, with consequent formation of $CH_3NH_2 \cdot HCl$ (Pibl.20).

The condensation reaction is run in the presence of caustic alkali at 65 - 70°. The resultant product, having a freezing point of 170 - 172° and a moisture of 10% is sent to explosives plant for nitration to tetryl.

Figure 67 illustrates the production of tetryl from dinitromonomethylamiline.

For safe nitration, dinitromonomethylaniline is converted to the sulfate salt. With this object, dinitromonomethylaniline is introduced into agitator (2), containing 2.5 times its quantity in sulfuric acid (96 - 98% H_2SO_4). The solution of the sulfate salt in sulfuric acid is delivered, simultaneously with the nitro mixture, into the major, continuous nitrator (6). The temperature in the major nitrator is held at 40°, and in the buffer nitrator 20°.

From the buffer nitrator (7), the reaction mixture goes, in sequence, to two vacuum hoppers (9). At the center of the vacuum hopper there is a discharge aperture with a cover atop it. Vacuum is employed to centrifuge the spent acid out of the vacuum hopper, and the tetryl is washed out with water through the central aperture into one of two agitators (10), with stirrers and a conical bottom. Here, the precipitate is mixed with water and the suspension is sent to vacuum-centrifuges (11), where the residue is centrifuged free of water and washed, first with soda solution, and then with water.

The spent acid contains approximately 60% H_2SO_4 and 7% HNO_3.

242 The raw tetryl is sent to recrystallization in another building. The recrystallizatic procedure is illustrated in Fig.68.

242 Two hundred liters of water are run into crystallizer (1), of stainless steel, from tank (7); 80 - 90 liters of acetone are run into tank (2), and the raw tetryl is run into tank (3) (onto a sieve at its bottom). The acetone from tank (2) is drained into crystallizer (1) (over the water) and heated to boiling. The acetone vapors are sent to condenser (4) from which the condensate is discharged to a tank (3), where the acetone dissolves tetryl, and the solution flows to a crystallizer. After solution of

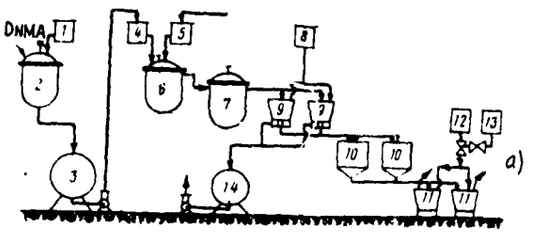


Fig.67 - Diagram of Production of Tetryl from Dinitromonomethylaniline (DNMA)
1- Commercial sulfuric acid metering tank; 2 and 10 - Agitators; 3 - Sulfate receiver; 4 - Sulfate metering tank; 5 - Mixed-acid metering tank; 6 - Main nitrator; 7 - Buffer nitrator; 8 and 12 - Water tanks; 9 and 11 - Vacuum filters; 13 - Tank for soda solution; 14 - Spent acid collector
a) Tetryl to crystallization

all the tetryl, which occurs in about 3.5 hrs, the acetone is sent from the condenser to tank (2), and heating is continued until it is completely driven out of the crystallizer. The contents of the crystallizer are then cooled to 20°. The driving off and cooling take about 1.5 - 2 hrs. Then, a little soda is added to the crystallizer (1), and the mass is sent to a vacuum filter (5) where the tetryl is filtered off. The filtered water from receiver (6) is sent to tank (7) and reused. The filtered and washed tetryl is dried at 70° over a period of 15 - 18 hrs.

The melting point of the product is 129.5°.

242 Safety. Tetryl manufacture is dangerous. XXXXXXXXXXXXXXX

The nitration of dimethylaniline sulfate is accompanied by the considerable heat effect. A sudden rise in temperature due to cessation in agitation or cooling will usually terminate in the expulsion of the mixture from the nitrator, and in its ignition. Should the temperature drop, the rate of nitration is sharply reduced, and the conditions arise for sudden development of an exothermic reaction (due to accumulation of unreacted components), which often terminates in ignition of the mass.

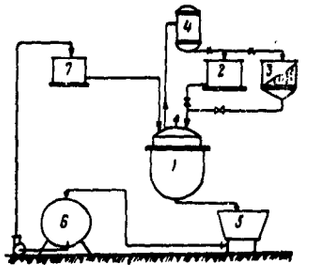


Fig.68 - Diagram of Recrystallization of Tetryl from Acetone
1 - Crystallizer; 2 - Tank for acetone; 3 - Tank for tetryl; 4 - Condenser; 5 - Vacuum filter; 6 - Receiver for water; 7 - Tank for water

Prevention of these phenomena requires that acceleration of run-in of components to the nitrator to a speed inducing a rise in temperature above the permissible level be prohibited. It is necessary to maintain a proper relationship

243 among the components delivered into the nitrator. If the temperature rise is greater XXXXthan that established in terms of a technical process, run-in has to be stopped XXXXXXXXXXX immediately, and cooling intensified. If these measures do not suffice to stop the rising temperature, it is necessary immediately to dump the nitrator contents into an emergency vat already full of water.

The nitration shop must have good ventilation of the processes, inasmuch as a large quantity of dangerous gases (nitrogen oxides, XXXXXXX dimethylaniline fumes) is liberated in the course of the work.

Unpurified raw tetryl has little XXX stability. Among other things, this renders

XXX

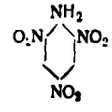
243 difficult nitration in continuous-action apparatus. Whereas, in batch-type work, the nitrator, and the other apparatus are carefully washed free of products after each operation, in continuous apparatus, some portion of the tetryl will be retained for a considerable period on such portions of the apparatus as the coils, the upper portion of the inner surface of the nitrator, the cover, etc. In the course of time, this product will decompose and may even ignite. Thus far, periodic stoppage of continuous-action systems for washing and cleansing of all apparatus continues to be a realistic method of combating this phenomenon.

The process of crystallization of tetryl is also dangerous, and it particularly pertains to crystallization out of acetone, which is highly combustible and may create explosive mixtures with air.

Before repair, it is necessary to clean and wash the apparatus carefully. The possibility of flame must be eliminated completely in the shop, and therefore there must be dependable insulation of wires. Motors must be installed in a different building, and illumination should be from without.

Section 3. Tetryl Analogs

2,4,6-Trinitroaniline (picramide)



is a hygroscopic crystalline substance, yellow in color, with a melting point of 192 - 195°.

Production of trinitroaniline begins with ortho- or para-nitroaniline, which is dissolved in 10 parts 95% sulfuric acid by weight and then nitrated with a mixture cohsisting of 1.5 part potassium nitrate by weight, and 10 parts 95% sulfuric acid.

243 Nitration is performed at a temperature of 0 - 5°. When run-in is completed, the mass is left until the next day and then 4.5 ltr saturated table salt solution is added at 0°. The picramide comes down as fine crystals. It is centrifuged out and washed with water. The yield of product is about 80% of the theoretical. The low yield is due to partial hydrolysis of the product, in the course of which ammonia and picric acid, which are comparatively readily soluble in water, are formed:

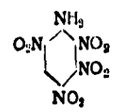
$$C_6H_2(NO_2)_3NH_2 + H_2O \rightarrow C_6H_2(NO_2)_3OH + NH_3.$$

Picramide may also be obtained from aniline by preliminary conversion thereof into acetanilide $C_6H_5NH\text{-}COCH_3$, in the nitration of which the metanitro derivative is not obtained as occurs in the nitration of aniline in sulfuric acid solution.

The explosive properties of picramide are: volume of gaseous explosion products 724 ltr/kg, heat of explosion 990 cal/kg, Trauzl block expansion 296 cc.

Trinitroaniline approximates trinitroanisole as an explosive, but is considerably inferior to tetryl (Bitl.30). Picramide has no practical application at the present time.

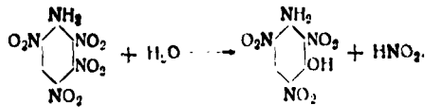
244 2,3,4,6-Tetranitroaniline



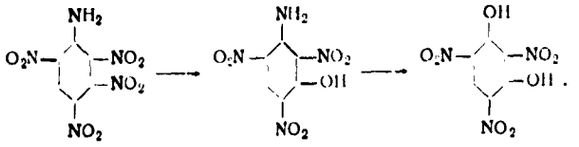
is a yellow crystalline product which decomposes upon fusion at 217 - 220°, and has a specific gravity of 1.667. A density of 1.68 is attainable by pressing. Tetranitroaniline is virtually non-hygroscopic, insoluble in water, and poorly soluble in the common solvents, and can be recrystallized from nitroxylene.

At room temperature, water virtually fails to react with tetranitroaniline, but at 50°, the reaction goes at a noticeable velocity, while upon boiling, conversion into

244 trinitroaminophenol goes quite energetically:



Heating with ethyl alcohol results in the formation of trinitroaminophenetol. The nitro group in the meta-position is instantaneously and completely detached at room temperature in an aqueous acetone solution of sodium acetate, also resulting in the formation of trinitroaminophenol. When KOH is reacted with trinitroaminophenol, trinitroresorcinol is formed:



The stability of tetranitroaniline is satisfactory. It will stand an Abel test at 71° for 1 hr. The tetranitroaniline manufactured during World War I was no longer useful after 9 years and further storage was dangerous.

The flash point is 222 - 223°. The shock sensitivity is considerably less than that of tetryl. Expansion in a Trauzl block is 430 cc, i.e. 10 - 15% higher than that of tetryl.

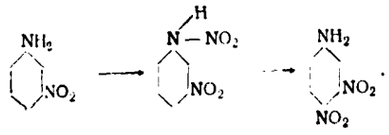
According to A.A.Solonina who made a detailed study of the properties of tetranitroaniline, it may serve as a substitute for tetryl (Bibl.23). A plant to manufacture tetranitroaniline for use in filling detonators was built in the USA during World War I.

According to the Flurscheim patent, tetranitroaniline is obtained from meta-nitroaniline by solution of 1 part thereof by weight in a mixture consisting of 3 parts KNO_3 by weight and 36 parts commercial sulfuric acid by weight at 68 - 70°.

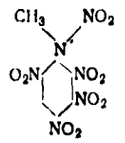
244 After the mixing of the components, the mass is held at a temperature of 100°. Then, (upon completion of the reaction), it is cooled to 20°, and the product is filtered. The product yield is 70% of the theoretical.

A.A.Solonina nitrated with nitric acid, having first dissolved the metanitroaniline in commercial sulfuric acid.

Nitration of the meta-nitroaniline with mixed acid goes through the stage of formation of nitrophenyl-N-nitroamine, which is then prearranged with dinitroaniline (Bibl.31):



245 2,3,4,6-Tetranitrophenylmethyl-N-nitroamine (meta-nitrotetryl)



was first obtained by van Romburgh in 1889 (Bibl.12) by dissolving dimethylaniline (1 part by weight) in commercial sulfuric acid (37 parts by weight) and then by pouring a mixture consisting of nitric acid (1.2 parts by weight 89.6% HNO_3) and commercial sulfuric acid (6 parts by weight) into the mixture cooled to -2°. The temperature during the run-in has to be -2°. The mixture is held at that temperature after the acid is run in. Under these conditions, it is chiefly meta- and para-nitrodimethylaniline that is formed. The large amount (37 times as much) of concentrated sulfuric acid facilitates an increase in the yield of meta-isomer, from which meta-nitrotetryl is obtained.

The solution resulting after holding is run into nitric acid (22.5 parts 89.6% HNO_3

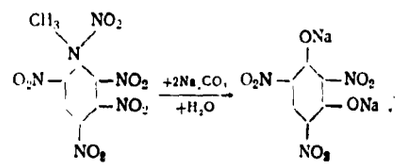
245 by weight) and held for a week. The meta-nitrotetryl which forms crystallizes out of solution, and the tetryl obtained simultaneously remains in the mother liquor.

The meta-nitrotetryl that has come down is separated from the solution, washed with water, and dried.

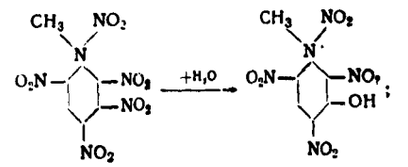
As already indicated above, meta-nitrotetryl can be obtained ~~X~~ under other conditions by the nitration of dimethylanilinesulfate (the conditions for production of tetryl). However, the main source of the formation thereof in this latter case is deemed to be an admixture of monomethylaniline in the initial dimethylaniline.

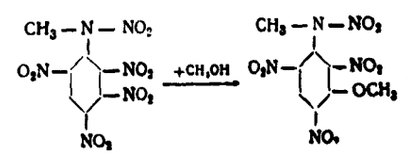
Meta-nitrotetryl is a white ~~X~~ crystalline substance with a yellowish tinge, having a melting point of 146°.

The nitro group in the meta-position is readily replaced by hydroxyl when the material is treated with water. In treatment with soda, both the nitro group in the meta-position and the nitro amine group undergo saponification, the consequence being a double sodium salt of styphnic acid:



Analogous reactions also occur under the effect of other reactants (Bibl.32):





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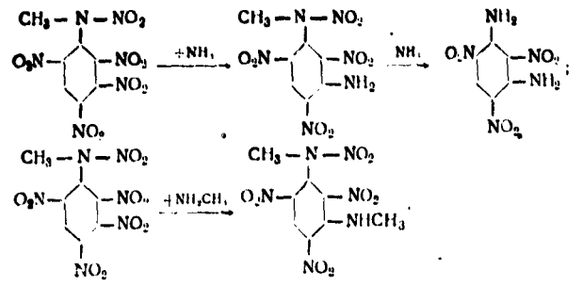
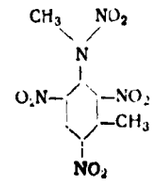


The reaction product of meta-nitrotetryl and water - trinitrooxyphenylmethylnitroamine is a colorless crystalline substance with a melting point of 187°. It is readily soluble in water, alcohol, benzene and ether. The presence of three nitro groups in the trinitrooxyphenylmethylnitroamine ring causes the hydrogen atom of the hydroxyl group to acquire acid characteristics. Upon reaction with metals, trinitrooxyphenylmethylnitroamine forms salts. Specifically, upon reaction with iron, it forms an iron salt in the form of a crystalline dark brown powder readily soluble in water, acetone, and alcohol, and insoluble in benzene, ether, and carbontetrachloride. When crystals of this salt are heated slowly, they carbonize without melting, and when they are heated rapidly they flash.

2,4,6-Trinitro-3-methylphenylmethyl-N-nitroamine (methyltetryl)



is a crystalline substance melting at 101°. It was first obtained by van Romburgh in 1876 (Bibl.33) by the nitration of dimethyl-meta-toluidine. Davis (Bibl.34) obtained it from the sodium salt of dinitrotoluenesulfonic acid:

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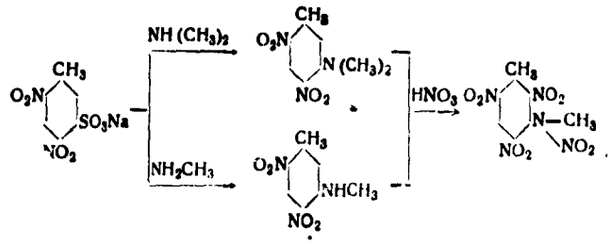
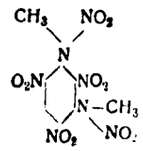


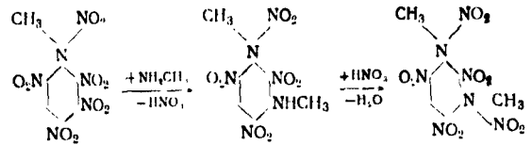
An analogous process was developed by T.Urbanski (Bibl.16).

Methyltetryl may also be obtained from the XXXXX wastes of trotyl production: sulfite caustics (see section "Trotyl Production").

2,4,6-Trinitro-1,3-di-(methyl-N-nitroamino)-benzene (ditetryl)

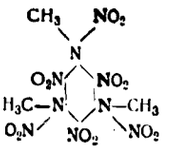


247 (or, more accurately, methyl-N-nitroaminotetryl) is a crystalline substance melting at 206°. It was first obtained by van Romburgh in 1887 (Bibl.35) by nitration of N,N'-dimethyl-meta-phenylenediamine. A more convenient method is that of obtaining it from tetranitromethyl-N-nitroamine, as developed by van Duyn (Bibl.32):

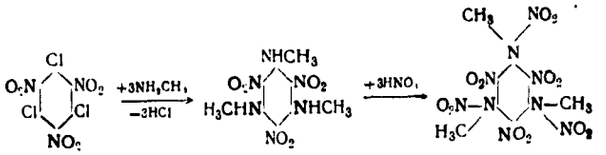


In its explosive properties, this substance is virtually equivalent to tetryl. However, it is more sensitive to mechanical effects. Ditetryl explodes when a 2 kg weight is dropped from 21 - 26 cm (for tetryl a height of 49 - 51 cm is required) (Bibl.16). The flash point of ditetryl is 214°.

2,4,6-Trinitrol-1,3,5-tri-(methyl-N-nitroamino)-benzene



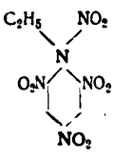
Tritetryl, or, more accurately, dimethyl-N-nitroamino-tetryl is a crystallized substance with a melting point of 280° (melts with decomposition). It was first obtained by Blanksma in 1908 (Bibl.36) by nitration of 2,4,6-trinitro-1,3,5-trimethylaminobenzene. In 1937, T.Urbanski (Bibl.37) suggested a method of producing tritetryl from trinitrotrichlorobenzene:



He also was responsible for determining the explosive properties of this product and showed that tritetryl is similar to tetryl.

Thus, despite the fact that the molecule of this substance has six nitro groups, as against four in the case of tetryl, no greater explosive property is observed.

2,4,6-Trinitrophenylethyl-N-nitroamine (ethyltetryl)

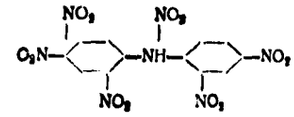


is a crystalline substance with a melting point of 96°. It was first obtained by van Romburgh in 1883 (Bibl.33) by nitration of ethylaniline. In its properties, this product is similar to tetryl (its explosive characteristics are somewhat lower). Medard (Bibl.38) showed the fugacity of ethyltetryl to be 1.04 times that of picric acid.

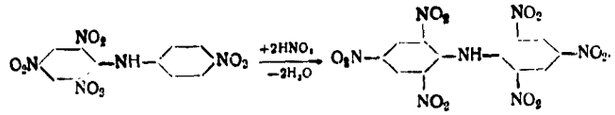
Ethyltetryl may be produced by condensation of dinitrochlorobenzene with

247 monoethylamine and subsequent nitration of the dinitro compound obtained by mixed sulfuric and nitric acid (50 - 60% H_2SO_4 and 40 - 50% HNO_3) at 40 - 50° (Bibl.39).

Section 4. Hexanitrodiphenylamine (Hexyl)

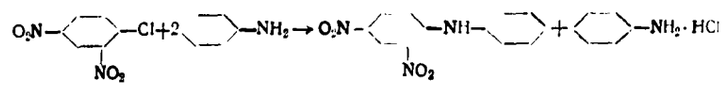
Hexanitrodiphenylamine  was first obtained by

Austen in 1874 by nitration of picril-para-nitroaniline:



Gnehm obtained it by nitration of diphenylamine. These methods have not found practical application because of the high cost of the hexyl.

In 1913, Carter worked out the method that has found practical application, based on reaction of 2,4-dinitrochlorobenzene with aniline, resulting in dinitrodiphenylamine:



Nitration of this product with nitric acid yields hexyl. The production of hexyl was begun in Germany in 1915, with the use of this method.

In 1920, Marshall in the USA suggested that hexyl be produced by treatment of dinitrodiphenylamine with mixed sulfuric and nitric acid.

Properties of hexyl. Hexyl is a yellow crystalline powder with a melting point of 245° (and it decomposes on melting).

Hexyl is not soluble in the usual solvents or in water. It hygroscopicity is 0.09%. It is capable of being recrystallized from acetone, glacial acetic, and concentrated nitric acids.

248 Because of the presence of six nitro groups, the hydrogen atom in the amino group is acid in character, and this is expressed in the fact that it is capable of being replaced by a metal, i.e., hexyl behaves as an acid (Bibl.40, 41). Metallic salts thereof may be obtained by heating aqueous or alcohol solutions of metal hydroxides or carbonates with hexyl suspended in these solutions. The metal salts are, except for the ammonia and magnesium salts, more sensitive to mechanical effects than is hexyl. The lead salt is the most sensitive. However, in view of the fact that hexyl is virtually insoluble in water, the formation of salts is of little probability under normal conditions.

Hexyl turns brown under solar irradiation. Its stability is somewhat less than that of trotyl, but higher than that of tetryl. The flash point is also higher than that of tetryl, and is 250°. Shock sensitivity is less than that of tetryl, but somewhat higher than that of picric acid. Hexyl is more sensitive to detonation than tetryl. The maximum initiating charge (a mixture of mercury fulminate and potassium chlorate) is 0.18 gm for hexyl, and 0.20 gm for tetryl. The volume of gaseous explosion products is 775 ltr/kg, the heat of explosion is 1080 kcal/kg, the brisance is 4.9 mm due to Kast, and the fugacity is 320 cc.. The velocity of detonation of hexyl (at a density of 1.60) is 7145 m/sec.

The effect of hexyl upon the skin is to cause dermatitis. Hexyl dust irritates the mucous membranes of the mouth and nose, and affects the lungs.

During the First World War, hexyl was employed with trotyl to fill naval munitions, as a mixture of the following composition: 30 - 40% trotyl and 60 - 70% hexyl. The density of these mixtures was 1.64 - 1.70. In the USA, the proposal was advanced that hexyl be used for detonators instead of tetryl. During the Second World War, hexyl was

249 manufactured in some small quantity only in Germany, where it was employed in a mixture with trotyl and aluminum to fill naval munitions (torpedoes and submarine mines). The explosive properties of these mixtures are presented in Table 79.

Table 79

a)	b)	c)	d)	e)	f)	g)	h)
60/24/16	85	1,73	6840	610	1400	408	4,2
67/8/25	85	1,81	6600	468	1665	358	4,4

a) Mixture (trotyl-hexyl-aluminum); b) Temperature of filling, °C; c) Density, gm/cc; d) Velocity of detonation, m/sec; e) Volume of gases, ltr/kg; f) Heat of explosion, kcal/kg; g) Fugacity, cc; h) Brisance due to Kast, mm

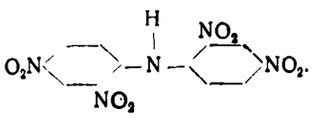
Production of hexyl. Hexyl may be obtained by nitration of diphenylamine in one or two stages. In the former instance, the diphenylamine is dissolved in sulfuric acid, and the resultant solution is slowly run into concentrated nitric acid. In the second case, nitration is run in two stages, the first employing a mixed acid consisting of 60% HNO_3; 20% H_2SO_4; 20% H_2O, whereas the second stage uses a mixture consisting of 73% HNO_3; 25% H_2SO_4; 2% H_2O (Bibl.42).

When hexyl is produced on an industrial scale, the starting substances are dinitrochlorobenzene and aniline, condensation of which yields dinitrodiphenylamine. The resultant product is nitrated in two stages to hexyl.

These processes were developed in Germany by Carter and in the USA by Marshall. According to Carter's method, alcohol is used as the medium for condensation (2.5 parts alcohol by weight per part of dinitrochlorobenzene). Two moles of aniline (1 mole going to neutralize HCl) is used per mole of dinitrochlorobenzene. Toward the end of the reaction, the mass becomes thick and takes on a dark red color. Then, water

249 is added, neutralization with chalk is performed, and, after filtration, the mixture is washed with water. The result is dinitrodiphenylamine with a melting point of 150 - 154° (the pure substance melts at 156 - 157°).

Nitration to tetranitrodiphenylamine is performed with 52% nitric acid (8 parts by weight per part of product by weight). Delivery of the nitro product into the nitric acid was begun at 40°, and ended at 90 - 100°. Upon cooling, the tetranitrodiphenylamine dissolved in the hot HNO_3 came down:



Nitration of the tetranitro product to hexyl is performed with 98% nitric acid in eight-fold the weight of the product. Mixture of the components begins at 40° and ends at 90°. Hexyl is separated from the spent acid on suction filters. Washing of the hexyl with water is also conducted in this equipment. After the washing, the hexyl is centrifuged free of water and dried at 70° for 36 - 48 hrs.

Under Marshall's method, condensation is performed in water. Toward this end, 2 moles of aniline and 1 mole of dinitrochlorobenzene are suspended in water heated to 60°, in three-fold the weight of the combined chemicals. The mixture is heated,

250 with continuous agitation, at 80°, for 1 hr. The dinitrodiphenylamine forms as large clumps of red spicular crystals. For complete solution of the aniline hydrochloride, the mass is stirred for another half hour at 80°. The resultant dinitrodiphenylamine is filtered, washed with dilute hydrochloric acid, then with water, and dried. The resultant product has a melting point of 148 - 152°.

Nitration is performed with a mixture of sulfuric and nitric acids. One part dinitrodiphenylamine is added, at 70°, to four parts mixed acid of the following

250 composition: 30 - 45% HNO_3 and 40 - 50% H_2SO_4. It is then held that 80 - 90°, at the conclusion of which the mass is cooled and filtered. The result is an amorphous substance of yellow-brown color, which is nitrated to hexanitro compound by mixed acid consisting of 60% HNO_3 and 40% H_2SO_4, 3.75 parts mixed acid by weight being employed per part tetranitro product by weight. Mixture of the components is performed at 70°, and it is held at 90°. The product is filtered, washed, and dried. The hexyl obtained has a melting point of 238.5 - 239.5°.

Depending upon the method of production, the hexyl may be loose, dense, or finely crystalline.

B. Hexogen and Other Nitro Derivatives of the Heterocyclic Amines

Hexogen or cyclotrimethylenetrinitroamine, along with PTEN, is one of the most powerful explosives used in minitions in World War II by all the warring countries. The reason for this is its high brisance and the stability of hexogen, a relatively

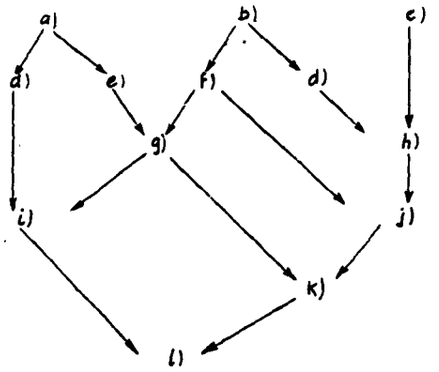


Fig.69 -

a) Air; b) Water; c) Coal; d) Oxygen; e) Nitrogen; f) Hydrogen; g) Ammonia (NH_3); h) Carbon monoxide (CO); i) Nitric acid (HNO_3); j) Formaldehyde (CH_2O); k) Urotropine [$(CH_2)_6 N_4$]; l) Hexogen [$(CH_2NNO_2)_3$]

250 simple production technology, and a virtually unlimited supply of raw materials, inasmuch as the raw materials - urotropine and nitric acid are ultimately produced from coal, air, and water, as is shown in Fig.69.

Hexogen was first obtained in 1897 by Lenze. In 1899, Henning (Bibl.43) took out a patent for a method of producing it via urotropine dinitrate, in the belief that hexogen would necessarily have to have pharmaceutical properties. In 1920 Herz (Bibl.44) suggested that hexogen be produced by direct nitration of urotropine with concentrated nitric acid, and showed that it is an explosive. Since that day, investigations of methods of production of hexogen and study of its explosive properties have continued.

251 As early as 1932 - 1933, production of hexogen by the Herz method in continuous-process installations was begun in England (Bibl.45) and apparently in other countries as well. In subsequent years and, particularly during World War II, additional methods of producing hexogen were developed.

The production of hexogen during World War II attained 360 tons per day in England (Bibl.45), 350 tons per day in the USA, 334 tons per day in Germany. During World War II as a whole, Germany produced a total of 113,000 tons of hexogen (Bibl.46).

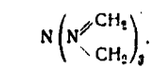
In Japan (Bibl.47), hexogen was employed in a mixture with trinitroanisole (60% trinitroanisole and 40% hexogen). Hexogen was employed in mixtures with other explosives in various types of munitions; artillery shells, aviation shells, submarine mines, and torpedoes. The majority of ersatz explosives contained from 10 - 30% hexogen.

Section 1. Chemistry of Production, Properties and Applications of Hexogen

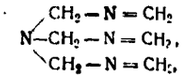
Hexogen may be obtained by nitrolysis of hexamethylenetetramine, or urotropine ($C_6H_{12}N_4$).

synthesized

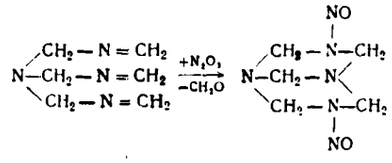
252 This last was ~~discovered~~ by Butlerov in 1859. He believed urotropine to have the following structure:



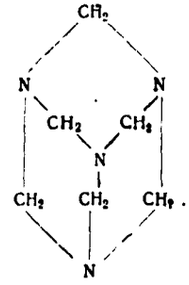
Later, Lozekan, proposed the following structure for urotropine, on the basis of the structure of the product of reaction between urotropine and nitrogen oxides, which proved to be dinitrosopentamethylenetetramine:



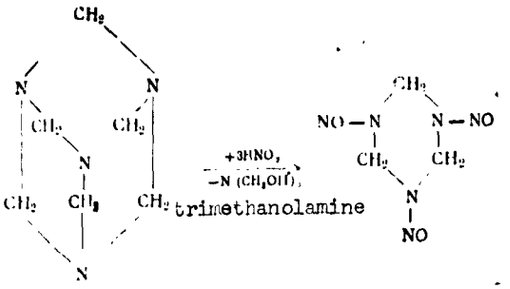
and that the reaction between urotropine and nitrogen oxides proceeded in accordance with the following mechanism (Bibl.48)



Duden and Scharf, like Lozekan, hold that all the nitrogen atoms in the urotropine molecule are of the same type - trivalent, but that they are not in a single plane, rather in the corners of a right tetrahedron:

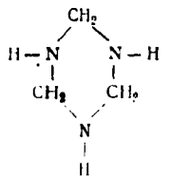


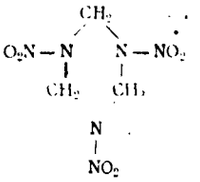
25[illegible] This is confirmed by the reaction between urotropine and nitric acid, resulting in the formation of trinitrosocyclotrimethylenetriamine:



According to Bachman (Bibl.49,50), a medium of pH = 3 is required for the formation of dinitrosopentamethylenetetramine, while a medium of pH = 1 is required in order to obtain trinitrosocyclotrimethylenetriamine.

Studies of the structure of the crystal lattice of hexamethylenetetramine confirm the correctness of the Duden and Sharf formula, by means of which one may arrive at the structural formula of hexogen. Under these circumstances, hexogen may be regarded as a derivative of a hypothetical cyclotrimethylenetriamine:


cyclotrimethylenetriamine


cyclotrimethelenetrinitroamine

Urotropine is a white crystalline powder, sweet to the taste. It is stable upon storage in air. When heated to over 100°, a small quantity volatilizes with partial decomposition, and methylamine is formed. In vacuum, volatilization occurs at 230 - 270°, virtually without decomposition. The solubility of urotropine at 20° in various solvents is adduced in Table 80.

252

Table 80

Solvent	Solubility of Urotropine, in gm, per 100 gm Solvent
Water	167
Absolute ethyl alcohol	2,89
90% ethyl alcohol	5,58
Benzene	0,23
Xylene	0,14

Urotropine is capable of reacting with hydrogen peroxide in the presence of citric acid, to form hexamethylenetriperoxidediamine:

$$C_6H_{12}N_4 + 3H_2O_2 \rightarrow N\begin{cases} CH_2-O-O-CH_2 \\ CH_2-O-O-CH_2 \\ CH_2-O-O-CH_2 \end{cases}N + 2NH_3.$$

253 When an aqueous solution of sodium nitrite and sulfuric acid are reacted with hexamethylenetetramine, dinitrosopentamethyle tetramine is produced (Bibl.51):

$$ON-N\begin{cases} CH_2-N-CH_2 \\ CH_2 \\ CH_2-N-CH_2 \end{cases}N-NO.$$

which is an unstable substance completely decomposable by water in accordance with the following mechanism:

$$C_5H_{10}N_6O_2 + 3H_2O \rightarrow 5CH_2O + 2NH_3 + 2N_2.$$

Urotropine is a weak base. With weak nitric and acetic acids, it forms salts, but sulfuric and hydrochloric acids decompose urotropine in accordance with the following equation

$$C_6H_{12}N_4 + 4H_2SO_4 + 6H_2O \rightarrow 6CH_2O + 4NH_4HSO_4.$$

Acetic acid yields a salt of the following composition: $C_6H_{12}N_4 \cdot 3CH_3COOH$.

Nitric acid in the form of a weak alcoholic solution forms urotropine nitrate $C_6H_{12}N_4 \cdot HNO_3$, a crystalline substance readily soluble in water. An aqueous solution

253 thereof is neutral in reaction. When weak nitric acid (50%) reacts upon an aqueous solution of urotropine, urotropine dinitrate $C_6H_{12}N_4 \cdot 2HNO_3$ is formed.

Urotropine dinitrate may be obtained in two ways:

1) one part urotropine by weight is dissolved in 2 parts water; the solution is cooled to 0 - 5°, and 0.9 part 65% nitric acid by weight is added thereto gradually, with agitation;

2) dry urotropine, one part by weight per 2.5 parts acid is added gradually to 35% nitric acid, with agitation and cooling (to 5°).

In both cases, a white crystalline precipitate of urotropine dinitrate comes down out of solution. It is filtered and washed with a 50% aqueous solution of alcohol and ether. Yield is 95% of theoretical.

Urotropine dinitrate has a melting point of 165° (it decomposes on melting). It is readily soluble in water. As a consequence of hydrolysis, the solution acquires a highly acid reaction and, when allowed to stand, decomposes with liberation of formaldehyde. Urotropine dinitrate is not soluble in alcohol, ether, chloroform, acetone, and carbontetrachloride.

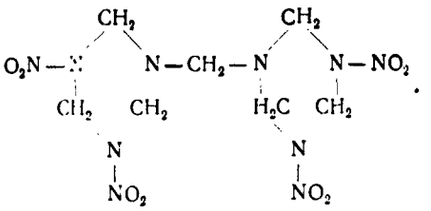
Urotropine dinitrate is an explosive, with a flash point of 190°, Trauzl block expansion of 190 cc, and a sensitivity to mechanical effects somewhat higher than that of trotyl.

The formation of urotropine dinitrate apparently occurs at all concentrations of nitric acid, and instantaneously, but in concentrated nitric acid it remains in solution, where it reacts with nitric acid, while in weak acid it crystallizes out of solution and leaves the zone of reaction.

253 Reaction of hexamethylenetetramine dinitrate and strong nitric acid at low temperatures (-50 to -60°) results in the formation of 1,3-dinitro-1,3,5-triaza-n-pentane nitrate

$$NO_2NH \cdot CH_2N(NO_2)CH_2 \cdot NH_2 \cdot HNO_3$$

and of methylenedi-1(3,5-dinitro-1,3,5-triaza-cyclohexane) (Bibl.52)



The solubility of the dinitrate in nitric acid depends upon the temperature and the concentration of the acid. In 20% HNO_3, its solubility is minimal, but at lower
254 and higher concentrations of nitric acid, it increases. When the concentration of HNO_3 is less than 10% and greater than 30%, the solubility of the dinitrate rises sharply.

In air, urotropine dinitrate decomposes slowly, and the nitric acid disintegrates. The dinitrate is hygroscopic. Its crystals contain about 20% water. In the drying of moist crystals, the nitric acid volatilizes along with the water of crystallization. Desiccation (dehydration) of the crystals is performed in practice by washing them with alcohol.

A higher yield of hexogen is attainable from urotropine dinitrate than from urotropine. Moreover, the concentration of the nitric acid, the module, and the nitrogen oxides content of the HNO_3 has less of an effect upon the hexogen yield.

When urotropine is nitrolized to hexogen by concentrated nitric acid, 88 kcal/mole of heat is emitted, but nitrolysis by the dinitrate is accompanied by the emission of

254 only 41.7 kcal/mole (Bibl.53).

Figure 70 illustrates the heat of reaction of ~~XXXXXXX~~ nitrolysis of urotropine and urotropine dinitrate with allowance for the heat of the side processes and of hydration when nitric acid of various concentrations is employed for nitrolysis (Bibl.54).

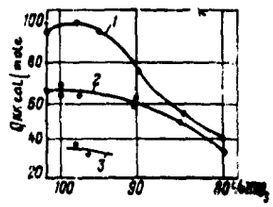


Fig.70 - Effect of Concentration of Nitric Acid upon Heat of Nitrolysis of Urotropine and Urotropine Dinitrate (DNU) (with Allowance for Heat of Side Processes and Hydration).
1 - Urotropine nitrolysis at 20°;
2 - Same at -35.5°; 3 - Urotropine dinitrate nitrolysis at -35.5°

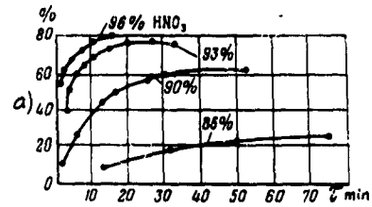


Fig.71 - Effect of Strength of Nitric Acid upon Rate of Hexogen Formation
a) Hexogen yield

An important advantage enjoyed by urotropine dinitrate ~~XXX~~ as intermediate product for the production of hexogen is the fact that ~~XXX~~ it may be obtained not only from urotropine, but also from formalin and ammonia, bypassing the stage involving separation of urotropine from solution, and drying thereof. A method has also been suggested for producing hexogen via urotropine dinitrate, in which the initial products are formalin, ammonia, and nitric acid. However, it has not gained application because of the solubility of urotropine dinitrate in water, and the inadequate stability.

254 Nitric acid, in 60 - 80% concentration, decomposes urotropine, and more concentrated acid converts it to hexogen. With increase in the HNO_3 concentration, the yield of hexogen increases (Fig.71) (Bibl.55). From this it follows that hexogen production requires the employment of nitric acid of not less than 93% concentration.

None of the velocity curves in Fig.71 reveal any period of induction. This demonstrates that the process rate is characterized by the speed of the nitrolysis reaction, and not by that of other processes.

The hexogen yield is significantly affected by nitrogen oxides, which give rise to oxidation of urotropine. If the nitric acid contains about 4% nitrogen oxides, the urotropine will burn out completely, and hexogen will not form at all. Therefore, nitric acid containing not more than 0.5% nitrogen oxides is employed for nitrolysis.

The optimum temperature of urotropine nitrolysis by nitric acid is 10 - 20°, and an increase therein makes for oxidizing processes and leads to a reduction in
25 the hexogen yield. The maximum yield when this reaction occurs is about 80%, in terms of urotropine.

A yield of 83% has been obtained by conducting the process very carefully and following the rate of urotropine addition (to eliminate local decomposition). The process was run with 21 moles 99.5 - 99.9% HNO_3 per 1 mole of urotropine at 20 - 25°, for more than 30 min. Upon completion of the mixing of the components, the reaction mixture was decanted into water (Bibl.49).

It has been established (Bibl.56) that the rate of nitrolysis of hexamethylenetetramine by nitric acid increases with increase in the modulus. Figure 72 illustrates the effect of the $\frac{HNO_3}{C_6H_{12}N_4}$ ratio on the hexogen yield (Bibl.56). At all concentrations of nitric acid, up to 88%, maximum yields of hexogen (about 80%)

255 were attained on the condition that an adequate molar ratio $\frac{HNO_3}{C_6H_{12}N_4}$ was adhered to. The minimum molar ratio for maximum yield rises approximately from 26:1 with 97% acid XXX to 110:1 with 88% acid.

If the molar ratio $\frac{HNO_3}{C_6H_{12}N_4}$ is selected accordingly, one may obtain identical nitrolysis rate with nitric acids of various concentrations, as is evident from Fig.73, which shows the rate of hexogen formation at 0° and various concentrations of nitric acid.

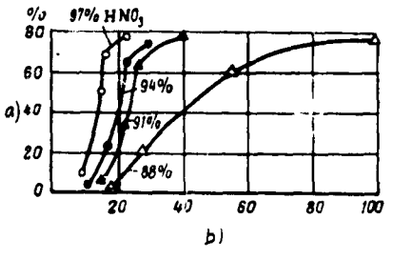


Fig.72 - Effect of $\frac{HNO_3}{C_6H_{12}N_4}$ Ratio upon Hexogen Yield

a) Hexogen yield; b) Molar ratio $\frac{HNO_3}{C_6H_{12}N_4}$

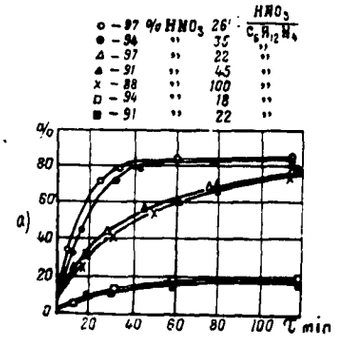


Fig.73 - Effect of $\frac{HNO_3}{C_6H_{12}N_4}$ Ratio upon Hexogen Formation Speed

a) Hexogen yield

At very large ratios $\frac{HNO_3}{C_6H_{12}N_4}$, the yield of hexogen is directly proportional to the amount of urotropine employed, and is not dependent upon the strength of the nitric acid (more than 88% HNO_3). Figure 74 illustrates this ratio, and it is assumed that one mole of hexogen is formed from three moles of HNO_3.

In practice, high molar ratios $\frac{HNO_3}{C_6H_{12}N_4}$ rapidly increase the cost of hexogen, and therefore urotropine nitrolysis is performed at a molar ratio of 22 - 24, corresponding to 11 - 12 parts 98% nitric acid by weight per 1 part urotropine. This amount of nitric acid does not result in

maximum yield, but an increase therein by increase in nitric acid consumption is economically undesirable.

On the basis of the fact that the maximum yield of hexogen is achieved only with a large excess of nitric acid, and that this excess increases sharply with reduction in the concentration of the acid, A.Vroom and C.Winkler (Bibl.56) concluded that the concentration of the active nitrating agent in the acid is not great and increases with reduction in the concentration of acid. These writers hold that the active nitrating agent is the nitrate cation of "nitrocidium", the $NO(OH)_2^{(+)}$ ion, formed from bimolecular HNO_3 in accordance with equation

$$ON\begin{matrix}O-H\ldots O\\ O\ldots H-O\end{matrix}NO \rightleftarrows \left[ON\begin{matrix}OH\\ OH\end{matrix}\right]^{\oplus} + NO_3^{\ominus}.$$

In support of this supposition they adduce a graph (Fig.75), in which the curve of the change in the concentration of the "nitrocidium" ion coincides with the curve of rate of formation of hexogen and various nitric acid concentrations.

Figure 75 illustrates the change in intensity of the infrared absorption band at 1.017 micron at HNO_3 concentration in accordance with the determinations of Dalmon and Freeman, who ascribed this band to associated molecules of acid.

Winkler (Bibl.57) comes to an analogous conclusion on the basis of an investigation of the nitrolysis of urotropine in acetic acid.

[illegible]

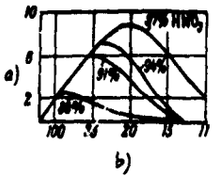


Fig.74 - Effect of $HNO_3/C_6H_{12}N_4$ Ratio on Yield of Hexogen in Terms of Nitric Acid Consumed

a) Hexogen yield with respect to HNO_3; b) Molar ratio $\frac{HNO_3}{C_6H_{12}N_4}$

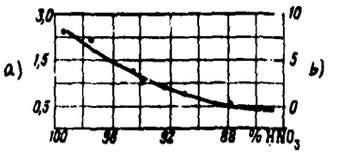


Fig.75 - Effect of Strength of Nitric Acid upon Concentration of "Nitrocidium " Ion and Initial Rate of Hexogen Formation.

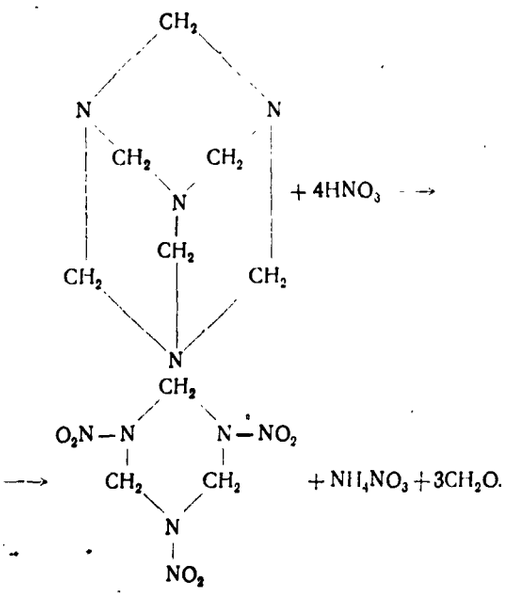
The hollow circles are the Dalmon and Freeman values taken as indices of the concentration of the "nitrocidium " ion. The solid circles are the initial rate of formation of hexogen at

$$\frac{HNO_3}{C_6H_{12}N_4} = \frac{40}{0} \text{ and } t = 0°.$$

a) Brightness of 1.017 micron absorption band;

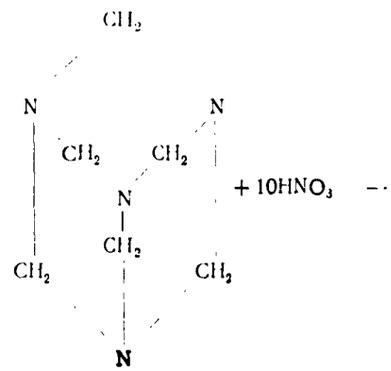
b) Rate in $\frac{\%}{\text{min}}$

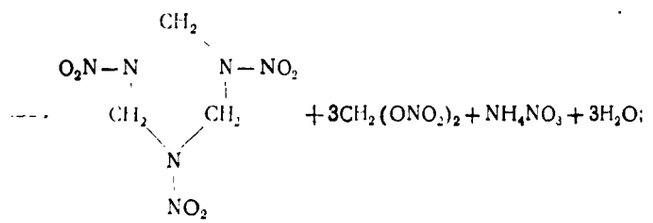
The ~~XXX~~ urotropine nitrolysis reaction may be written in its general form as follows:

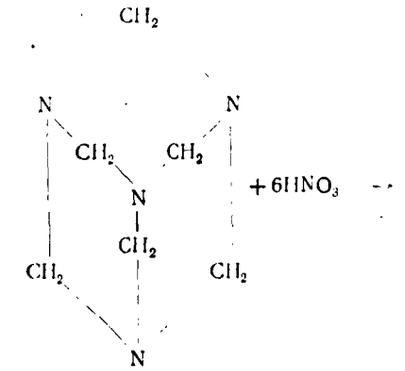


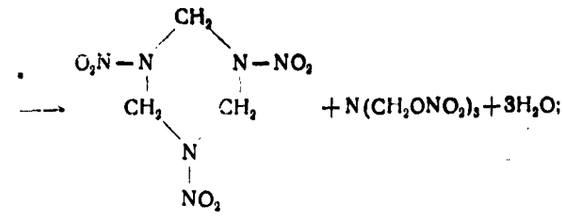
257 However, the small yield of hexogen and the large consumption of nitric acid testify to the fact that this reaction is considerably more complex and is accompanied by side processes.

Hale and others (Bibl.58) hold that the hydrolysis of urotropine is such a process. An investigation of the side products formed on the synthesis of hexogen has demonstrated the presence of a certain amount of methylene dinitrate $CH_2(ONO_2)_2$ and trimethanolamine nitrate $N(CH_2ONO_2)_2$ in the concentrated spent acid. On the basis thereof it is assumed that urotropine nitrolysis proceeds in accordance with the following mechanisms:

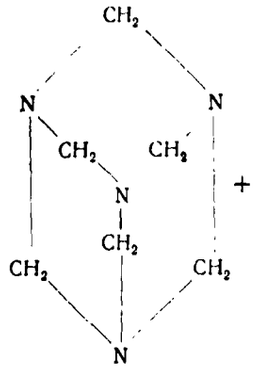








$$\longrightarrow \quad + N(CH_2ONO_2)_3 + 3H_2O;$$



$$+ 8HNO_3 \rightarrow 2N(CH_2ONO_2)_3 + 2NH_4NO_3.$$

The intermediate products are comparatively stable in concentrated spent acid, but when allowed to settle or, particularly, upon dilution with water, they undergo saponification:

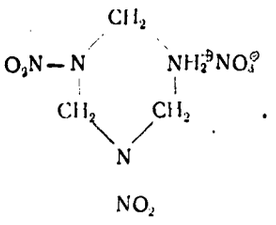
$$CH_2(ONO_2)_2 + H_2O \rightarrow CH_2O + 2HNO_3;$$
$$N(CH_2ONO_2)_3 + 3H_2O \rightarrow 3CH_2O + 2HNO_3 + NH_4NO_3.$$

Formaldehyde is detected in dilute acid by its odor and may readily be driven off the neutralized solution with heating.

The most recent investigations do not confirm the mechanisms presented above. It was found that the side products XX differ in that XXXX composition, and the process itself goes stepwise.

Vroom and Winkler (Bibl.56), performing the nitrolysis of urotropine with 97% nitric acid at -40°, obtained a substance with a melting point of 98 - 99°,

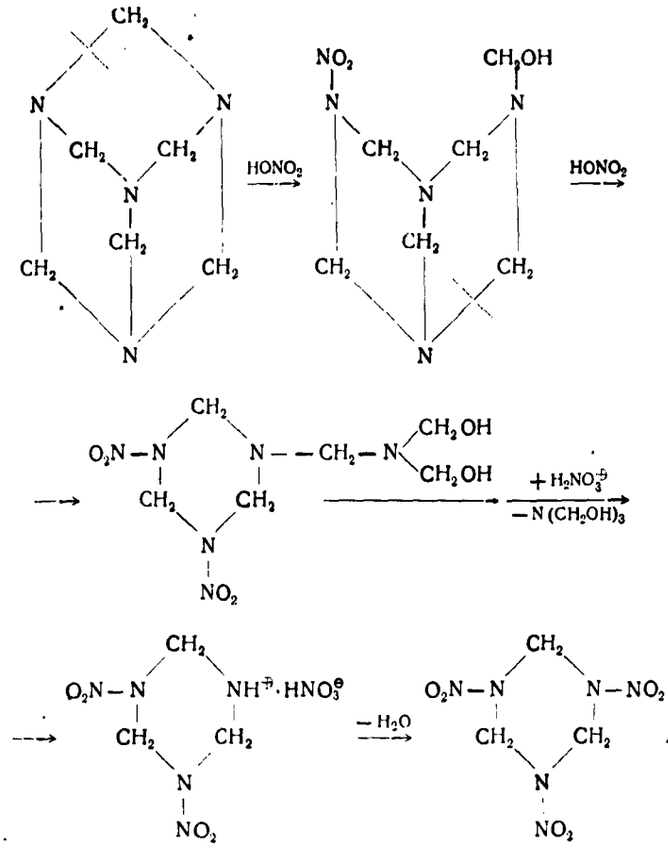
upon 94%
which converted to hexogen ~~XX~~ subsequent treatment with/nitric acid. Analysis showed that the substance is 3,5-dinitro-1,3,5-triazacyclohexane-1-nitrate (I):



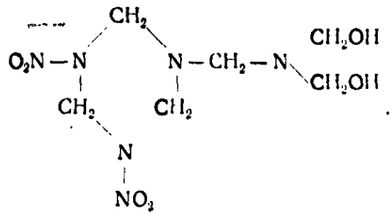
259 Conversion thereof into hexogen also was performed by treatment of suspension ~~XX~~ in nitromethane with boron fluoride or by treatment with P_2O_5 solution in 88% HNO_3.

3,5-Dinitro-1,3,5-triazacyclohexane-1-nitrate approximately equals hexogen ~~XXX~~ as explosive properties, and its shock sensitivity is somewhat higher than for hexogen.

The authors hold that 3,5-dinitro-1-,3-5-triazacyclohexane-1-nitrate is an by
intermediate in the nitrolysis of utropine/nitric acid, and that the final conversion speed.
thereof into hexogen ~~XX~~ characterizes the overall process ~~XXXX~~. This conversion is inhibited by the side products of reaction and may lead to complete decomposition of the intermediate product, resulting in a low hexogen ~~XXX~~ yield. The urotropine nitrolysis reaction mechanism is, according to these investigations, the following:

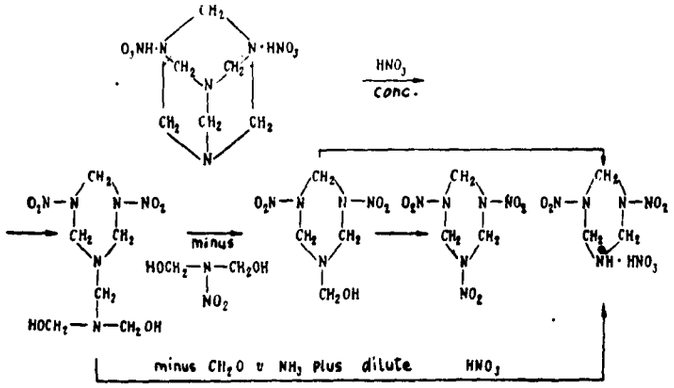


Berman and others (Bibl.59) do not believe the intermediate product in hexogen process to be 3,5-dinitro-1, 3,5triazachlorohexane-1-nitrate. According to their data, formation thereof occurs when the reaction mixture is diluted as a consequence of the decomposition of 1-dimethylolaminomethyl-1,3, 5-dinitro-1, 3,5-triazacyclohexane, the formula of which is

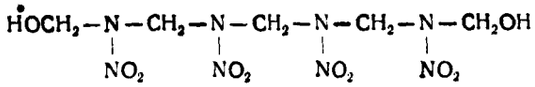


The composition of the latter in concentrated acid results in cleavage of the dimethylamine group with conversion thereof into dimethylol nitroamide, and the hexagonal ring yields 1-methylol-3,5-dinitro-1,3,5-triazacyclohexane. This last compound converts to hexogen, but may also yield 3,5-dinitro-1,3,5-triazacyclohexane-1-nitrate.

The process diagram looks like a series of nitration reactions of the ternary amine



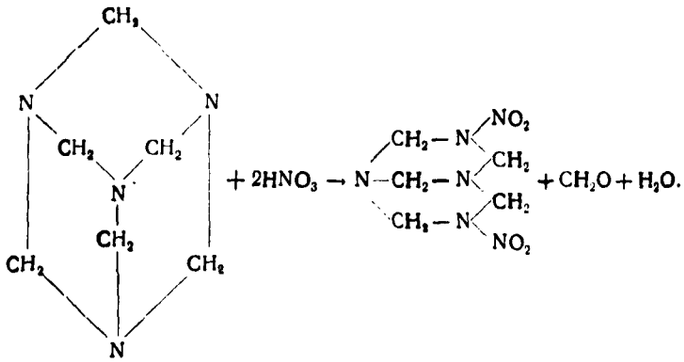
1-Dimethylolaminomethyl-3,5-dinitro-1, 3,5-triazacyclohexane yields an insignificant amount, upon decomposition, of the linear compound 1,9-dihydroxy-2, 4,6,8-tetranitro-2,4,6,8-tetrazanonane (dihydroxypentamethylenetetranitroamine):



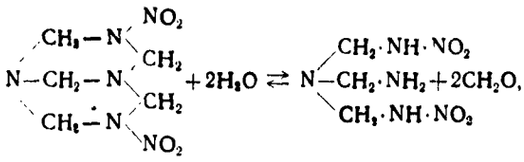
or, to be more exact, its nitrate ester.

Chute and associates (Bibl.55) have shown that when urotropine reacts with concentrated nitric acid, the consequence is not only hexogen but dinitropentamethylenetetramine (melting point 198°). Product yield rises with reduction in reaction time and increase in excess of HNO_3. The yields of dinitropentamethylenetetramine and hexogen are apparently mutually related. The authors assume that this is due to a single common initial compound which may possibly be utropine dinitrate, the primary formation of which in the reaction, whereby urotropine is nitrolysed to hexogen, has been demonstrated on the basis of comparison of the heats of nitrolysis of both products (Bibl.53,54).

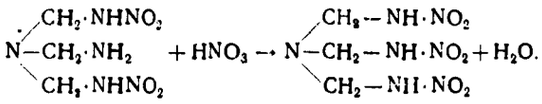
261 According to Cerrione (Bibl.46), the formation of dinitropentamethylenetetramine is the first side reaction in the nitrolysis of urotropine by concentrated nitric acid:



In a nitric acid solution, dinitropentamethylenetetramine behaves as a di-acid base and is converted, to begin with, to the primary nitroamine:

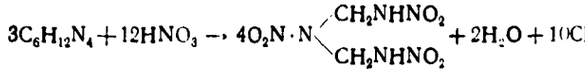


which then converts to dinitrotriaminotrimethylamine. Under given conditions of nitrolysis, this latter converts partially into trinitrotriaminotrimethylamine:



This substance is relatively stable in the cold, but at 60° it decomposes to yield formaldehyde and ammonia.

Simultaneous with the formation of dinitropentamethylenetetramine and its conversion products, urotropine nitrolysis is accompanied by the formation of trinitrodiaminodimethylamine (TDA) in accordance with the following reaction:



As distinct from the preceding one, this product does not dissolve in water. Therefore, when hexogen is separated from the nitro mass by dilution with water, trinitrodiaminodimethylamine is also liberated. This is an impurity in unstabilized hexogen. In some cases, this substance constitutes 10% of the whole.

262 Trinitrodiaminodimethylamine slowly goes into solution at low temperature, converting into soluble primary nitroamide - methylenedinitroamine:

$$O_2N\cdot N\begin{matrix}CH_2NHNO_2\\CH_2NHNO_2\end{matrix}\cdot CH_2\begin{matrix}NHNO_2\\NHNO_2\end{matrix}+CH_2O+N_2O.$$

At elevated temperature (75 - 80°), this process proceeds with more complete decomposition in accordance with the reaction:

$$C_2H_6N_6O_6 \rightarrow 2CH_2O+3N_2O+H_2O.$$

Therefore, what is termed the stabilization of hexogen is merely destruction of trinitrodiaminodimethylamine.

A third side product of urotropine nitrolysis is methylene nitroamine (or nitroiminomethane) $CH_2 = N \cdot NO_2$ (monomer of hexogen), which forms in accordance with the reaction

$$C_6H_{12}N_4+4HNO_3 \rightarrow 4CH_2=N\cdot NO_2+2CH_2O+2H_2O.$$

This compound exists only in solution and readily decomposes in accordance with the equation

$$CH_2=N\cdot NO_2 \rightarrow CH_2O+N_2O.$$

Cerrione regards hexogen as a trimer of methylene nitroamine, the greater chemical stability of which he ascribes to its cyclic structure.

Cerrione indicates the following conditions of formation of hexogen and the products accompanying it.

Hexogen is formed primarily at a 1:8 - 1:30 ratio urotropine to nitric acid (or a modulus of 8 - 30), acid concentration in access of 95%, and nitrolysis temperature over 10°. The product does not result if the modulus is less than 4

or more than 500, and if the concentration of nitric acid is less than 85%.

Trinitrodiaminodimethylamine forms primarily at a modulus of 8 - 20, a nitric acid concentration of more than 97%, and a temperature in excess of 10°, with a maximum yield of about 10%. The product is not obtained at a modulus of less than 4 or more than 500 and a concentration of acid less than 95%.

Dinitropentamethylaminetetramine is formed in more dilute acids. Maximum yield is achieved with 85% acid and a modulus of less than 10 (at a modulus of 3.5, the yield is 65%). The yield rises with reduction in the temperature of nitrolysis. Methylene nitroamine does not form if the concentration of nitric acid is less than 95% or if the modulus is less than 10. With rise in modulus to 300, more methylene nitroamine is formed than hexogen, and at a modulus of 700 - 800, the yield thereof attains 70% in terms of methylene groups. With rise in temperature, the product yield increases.

Thus, the yield of trinitrodiaminodimethylamine is determined, in practice, by the same parameters as the yield of hexogen. However, the maximum yield of this product is not great (10%). The conditions serving as an obstacle to the formation of dinitropentamethylenetetramine and increasing the yield of hexogen (concentrated acid at high modulus) are most favorable to the formation of methylene nitroamine, and vice versa. The maximum yield of hexogen is obtained under conditions in which the curves of evolution of yield of dinitropentamethylenetetramine and increase in yield of methylene nitroamine intersect. Simultaneous formation of dinitropentamethylenetetramine, methylene nitroamine, and hexogen, is a simple and convincing explanation of the low yield

of the latter, occurring upon nitrolysis of urotropine by nitric acid.

When weak nitric acid acts upon urotropine, the consequence is either hydrolysis (under the effects of 80 - 90% acid) or formation of a salt (acid concentration less than 80%). In the former instance, methylenediamine, triaminotrimethylamine, and diaminodimethylamine are formed (the maximum yield of these compounds achieves 80%) and in the second case it is urotropine dinitrate that is formed. At very low concentrations of HNO_3 (less than 15%), the yield of dinitrate diminishes as a consequence of its solubility in water.

Hexogen formed upon nitrolysis of urotropine will be almost entirely dissolved in the spent acid. To separate it out, the solution obtained has
263 to be diluted to an HNO_3 concentration of not more than 60%, at which the solubility of hexogen is quite negligible. Dilution with water may be performed in two ways: either by pouring the solution obtained into the necessary amount of water or by adding water to the hexogen solution.

When the first method is employed, hexogen is separated out in the form of very fine crystals. This greatly complicates further work therewith (it is difficult to filter it, and the filters clog). However, when the second method is used, the spent acid is diluted with the water gradually, and hexogen formation takes place less rapidly, making for the formation of larger crystals thereof.

This method is complicates somewhat by the circumstance that the spent acid contains, not only hexogen, but side products of the synthesis which decompose when diluted with water, as indicated above, to formaldehyde. Formaldehyde is vigorously oxidized by nitric acid at concentrations of 60 - 65% or more, and the

heat of reaction thus liberated is capable of heating the nitro mass (inducing the composition of the hexogen). Therefore, the dilution must be accompanied by careful adherence to the appropriate conditions of temperature.

In practice, this process is carried out in continuous apparatus (Bibl.45, 60), and as a consequence the hexogen solution is poured, simultaneous with the water diluting it, into an apparatus filled with dilute acid. The 50 - 60% spent acid obtained as the result of dilution is not stable, as it contains formaldehyde, which oxidizes readily under these conditions. In order to increase the stability of the spent acid, it is heated to 60 - 65°, at which temperature formaldehyde is completely oxidized to CO_2. In industry, stabilization of the spent acid by heating is performed simultaneous with dilution with water (Bibl.61).

Willson (Bibl.62) has patented a method of producing large hexogen crystals which flow well. The method consists of adding to the nitration mixture (produced by introducing urotropine into concentrated nitric acid) with agitation and at a temperature of 65 - 70°, weak (50 - 70%) nitric acid containing a little sodium nitrite. When the temperature, regulated by external cooling, rises, the side products begin to decompose. The gaseous products of the composition, containing a large quantity of nitrogen oxides, are removed through the system of ventilation and trapped in absorption equipment.

Destruction of the side product of the reaction, formaldehyde, by oxidation thereof with nitric acid is one of the weakest sides of this method. In actuality, the yield of hexogen from urotropine, computed on the formaldehyde (from which urotropine is produced) is only 35 - 40%. The rest is oxidized, and this is the cause of a large unproductive consumption of nitric acid.

This shortcoming is eliminated to some degree by the two-stage method of producing hexogen from urotropine or from formaldehyde (Bibl.63). In the first stage, urotropine is obtained by saturation of formalin (30% formaldehyde solution) with gaseous ammonia:

$$6CH_2O + 4NH_3 \rightleftarrows C_6H_{12}N_4 + 6H_2O.$$

Under these conditions, urotropine is produced in the form of a 20 - 25% solution. When weak nitric acid is added to the urotropine solution, the acid comes down out of solution, almost quantitatively, in the form of urotropine dinitrate:

$$C_6H_{12}N_4 + 2HNO_3 \rightarrow C_6H_{12}N_4 \cdot 2HNO_3.$$

Thus, the evaporation operation is replaced by the operation of precipitation, which is cheaper and more productive. It proved possible, on the same principle, to recover the formaldehyde from the spent acid. After washing and drying, the pressed crystals of urotropine dinitrate convert into hexogen for which only five
264 parts concentrated nitric acid are employed, by weight.

The hexogen yield from the dinitrate is approximately 5% larger than from urotropine. Moreover, the hexogen yield may be increased at the expense of the formaldehyde in the dilute spent acid. With this purpose, the spent acid is diluted at low temperature (15 - 20°), and then the acid is neutralized by ammonia to protect the formaldehyde from oxidation. The result is the formation of urotropine and ammonium nitrate:

$$6CH_2O + 4NH_3 \rightleftarrows C_6H_{12}N_4 + 6H_2O;$$
$$HNO_3 + NH_3 \rightarrow NH_4NO_3.$$

The urotropine is precipitated as urotropine dinitrate by weak nitric acid. The filtered spent acid is a 50% solution of ammonium nitrate and goes to evaporation.

In Germany, during World War II, various other methods (Bibl.47) were employed in addition to the major method of nitrolysis.

When hexogen was produced by the "W" method (suggested in 1934 by Wolfram), the raw material is formaldehyde which is converted, by a series of successive reactions, into potassium cyclotrimethylenetriimino sulfate, termed "white salt", and is then nitrated to hexogen. The following reactions occur herein:

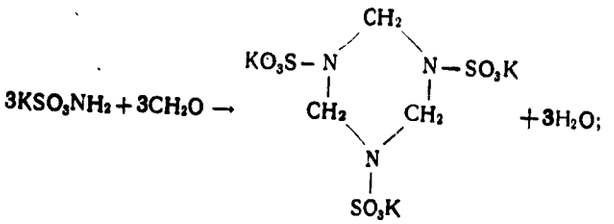
1) Sulfaminic acid is formed by the action of ammonia on sulfur anhydride:

$$SO_3 + NH_3 \rightarrow HSO_3NH_2;$$

2) Reaction of sulfaminic acid with potassium carbonate results in the formation of potassium sulfaminate:

$$2HSO_3NH_2 + K_2CO_3 \rightarrow 2KSO_3NH_2 + H_2O + CO_2;$$

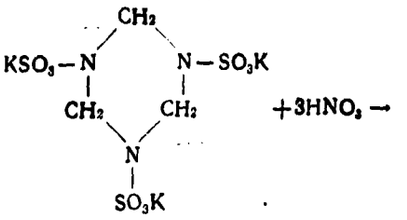
3) Further, condensation of the potassium sulfaminate with formaldehyde occurs to form "white salt":



$$3KSO_3NH_2 + 3CH_2O \rightarrow \text{(white salt)} + 3H_2O;$$

4) The action of concentrated mixed acid upon "white salt" results in

hexogen:



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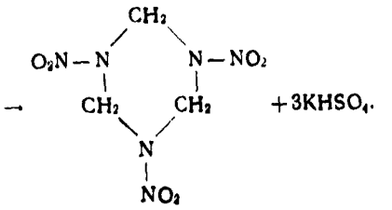
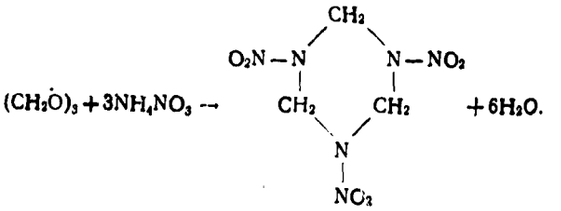


The hexogen yield is approximately 80%, in terms of the formaldehyde consumed.

The "E" method (its inventor was Elbe) is based on condensation of paraformaldehyde with ammonium nitrate to hexogen:



The reaction is performed in an acetic anhydride medium, in which pulverized paraformaldehyde and dry ammonium nitrate are introduced, with energetic agitation. The acetic anhydride takes up water, converting it to acetic acid.

The reaction goes better if boron fluoride is employed. This is

simultaneously a dehydrator and catalyst. The acetic anhydride is first saturated with boron fluoride, to form the compound $(CH_3CO)_2OBF_3$ (Bibl.64). However, this method results in hexogen having a low melting point, because it contains a large quantity (up to 20%) of impurities.

Hexamethylenetetramine dinitrate (Bibl.65) has been isolated from the reaction products of paraformaldehyde and ammonium nitrate in glacial acetic acid. The authors hold this to be an intermediate product in the formation of hexogen under these conditions.

The "K" method (due to Knoffler) consists of treating a mixture of urotropine and ammonium nitrate with concentrated sulfuric acid. Formation of the hexogen apparently proceeds in accordance with two reactions:

1) $C_6H_{12}N_4 + 4HNO_3 \rightarrow C_3H_6(NNO_2)_3 + 3CH_2O + NH_4NO_3$;
2) $3CH_2O + 3NH_4NO_3 \rightarrow C_3H_6(NNO_2)_3 + 6H_2O$,

or, in sum:

$$C_6H_{12}N_4 + 4HNO_3 + 2NH_4NO_3 \rightarrow 2C_3H_6(NNO_2)_3 + 6H_2O.$$

The yield of hexogen with respect to formaldehyde is 60%. A shortcoming of this method is the large consumption of nitric acid and ammonium nitrate that has to be metered in. This is because ammonium nitrate is not very good as a condensation medium.

When acetic anhydride is employed as the dehydrator, the conditions for condensation of formaldehyde and ammonium nitrate improve. Simultaneously, more complete conversion of HNO_3 to $NO_2^{\oplus}$, which is an active nitrating agent (Bibl.66), takes place. This method is called the "KA" method, as distinct from the preceding

one. There are two versions of this method.

In accordance with the first version, ammonium nitrate is suspended in acetic anhydride, and nitric acid and uretropine are added simultaneously to the suspension. An increase in yield is achieved by employing the dinitrate of urotropine for nitration, instead of urotropine itself.

The reaction goes in accordance with equation

$$C_6H_{12}N_4 \cdot 2HNO_3 + 2NH_4NO_3 + 2HNO_3 + 6(CH_3CO)_2O \rightarrow$$
$$\rightarrow 2C_3H_6(NNO_2)_3 + 12CH_3COOH + 118 \text{ Kcal/ mole}$$

As a consequence of the insignificant solubility of hexogen in acetic acid at 20°, the reaction mass is not diluted with water.

During World War II, hexogen was produced in the United States, Canada, and England, by Bachman-Ross methods, analogous to the German "KA" method. Nitrolysis of urotropine by nitric acid was performed in the presence of ammonium nitrate, acetic acid, and acetic anhydride. The technological procedure employed in the Bachman process differs somewhat from the "KA" method (Bibl.67, 68, 69, 70). According to Ross (Bibl.70) the formation of hexogen from urotropine occurs as follows:

$$C_6H_{12}N_4 + 4HNO_3 + 2NH_4NO_3 + 6(CH_3CO)_2O \rightarrow$$
$$\rightarrow 2C_3H_6(NNO_2)_3 + 12CH_3COOH;$$

in which 140 kcal/mole of heat is liberated (the energy of activation is 12 kcal).

The reaction occurs in a number of stages and is accompanied by the formation of side products which are capable, under given circumstances, of becoming the major products. The intermediate reaction product is apparently

urotropine mononitrate (Bibl.53, 71).

Urotropine goes into reaction almost instantaneously (within 5 sec at 35°) one molecule of hexogen being formed as a result. Addition of NH_4NO_3 results in the formation of a second molecule of hexogen (Bibl.72,73). This shows that the second molecule of hexogen is formed from the cleavage products of urotropine and ammonium nitrate.

Hexogen produced by the Bachman-Ross method contains up to 10% oxygen (tetranitrotetrazacyclooctane) (Bibl.74).

With the object of studying the mechanism of the reactions occurring, ammonium nitrate containing labeled nitrogen atom (N^{15}) in the ammonium group ($N^{15}H_4NO_3$) was employed. It was found that hexamethylenetetramine is subjected to two major types of decomposition, resulting in the formation of compounds containing three atoms of amine nitrogen (hexogen) and a compound containing four atoms of amine nitrogen (oxygen). If the medium is highly acid, and the nitrating agent is highly active, the consequence is cleavage of the former type, resulting in the formation of hexogen. If acidity is low, and activity of the nitrating agent is also, cleavage of the second type resulting in the production of oxygen occurs.

Thus, the hexogen-producing reaction is intimately related to the oxygen-producing reaction.

Epstein and Winkler (Bibl.75) determined the relationship of the hexogen and oxygen yield to the amount of NH_4NO_3 (Fig.76) introduced into the reaction. These authors hold that urotropine converts at least to two intermediate compounds, one

of these capable of serving as a source of hexogen and oxygen, while the other will yield hexogen only. Thus, if the NH_4NO_3 is added later, the hexogen yield is not more than 30%, while postponement of the introduction of NH_4NO_3 is not reflected in the oxygen yield.

The optimum yield of hexogen (70% $C_6H_{12}N_4 \rightarrow 2C_3H_6(NNO_2)_3$) occurs at a molar ratio of $C_6H_{12}N_4$: HNO_3 : $(CH_3CO)_2O$ 1:5.2 : 20 and 2.7 moles NH_4NO_3. Further increase in the amount of NH_4NO_3 has no practical effect upon the hexogen yield.

267 The optimum yield (25% $C_6H_{12}N_4 \rightarrow 1.\ C_4H_8(NNO_2)_4$) at the same ratios of $C_6H_{12}N_4$, HNO_3 and $(CH_3CO)_2O$ occurs in the presence of 2.3 moles NH_4NO_3.

The amount of nitric acid has a significant influence upon the yield of hexogen and oxygen. At a $C_6H_{12}N_4$:$(CH_3CO)_2O$:NH_4NO_3 = 1 : 20 : 3 ratio, the optimum yield of both products is obtained in the presence of 6 moles HNO_3 (Fig.77). Simultaneous increase in the amount of NH_4NO_3 shifts the optimum yield of hexogen and oxygen toward higher values (see Fig.76).

With increase in the amount of $(CH_3CO)_2O$, the yield of hexogen rises, and with the ratio $C_6H_{12}N_4$: HNO_3 : NH_4NO_3 = 1 : 5.2 : 3 achieves a maximum at 15 - 20 moles of $(CH_3CO)_2O$. Further increase in the amount of $(CH_3CO)_2O$ does not lead to an increase in the hexogen yield. The yield of oxygen is at a maximum at 15 moles of $(CH_3CO)_2O$ (see Fig.77).

Investigations serve as the basis for suggesting the following mechanism of urotropine nitrolysis by nitric acid in the presence of ammonium nitrate and acetic anhydride (Fig.78) (Bibl.75). Stages 5, 6, and 7 regulate the process rate

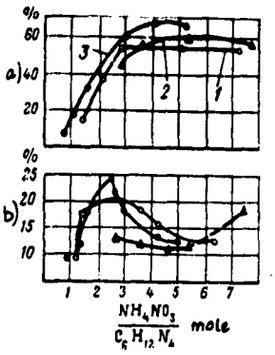


Fig.76 - Effect of Quantity of NH_4NO_3 upon Yield of Hexogen and Oxygen

Curve No.	Molar Ratios			
	CH_3COOH	HNO_3	$(CH_3CO)_2O$	$C_6H_{12}N_4$
1	194	5,2	20	1
2	194	9,5	20	1
3	104	5,2	20	1

a) Hexogen yield; b) Oxygen yield

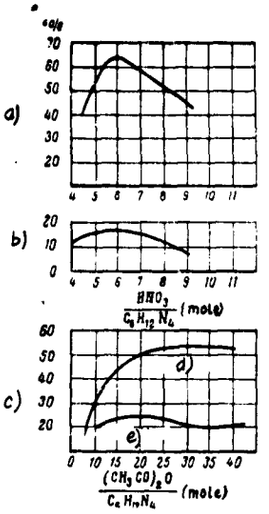
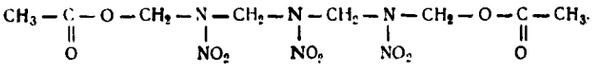


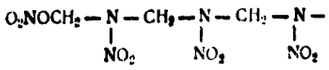
Fig.77 - Effect of Amount of HNO_3 and $(CH_3CO)_2O$ upon Yield of Hexogen and Oxygen

a) Hexogen yield; b) Oxygen yield; c) Yield of Hexogen and oxygen; d) Hexogen; e) Oxygen

in the production of hexogen under the Bachman-Ross reaction. If stage 5 is eliminated by slowing the ammonium nitrate addition reaction, the consequence is the formation of linear products, but there is no reduction in nitric acid consumption, inasmuch as, instead of hexogen, formation of diacetoxytetramethylene-dinitroamine occurs (Bibl.1), containing the same number of nitro groups:



Replacement of acetic anhydride by nitric acid anhydride (at a ratio of $C_6H_{12}N_4 : HNO_3 : N_2O_5 = 1 : 11.7 : 3.9$) leads to the formation of dinitrooxytetramethylenetrinitroamine (Bibl.55) in addition to the hexogen



268 Chute and others (Bibl.55) produced dinitropentamethylenetetramine by treating urotropine dinitrate with acetic anhydride for 4 days. Nitrolysis by the latter by a mixture of 99.6% nitric acid and NH_4NO_3 (in a molar ratio of 1.78 : 1) at 25° and 70 - 75° led to the formation of a mixture of 52% hexogen and 17% oxygen. Change in the ratio between HNO_3 and NH_4NO_3 to 1 : 1 increases the yield of hexogen to 57%, and the yield of oxygen is diminished accordingly (Bibl.76):

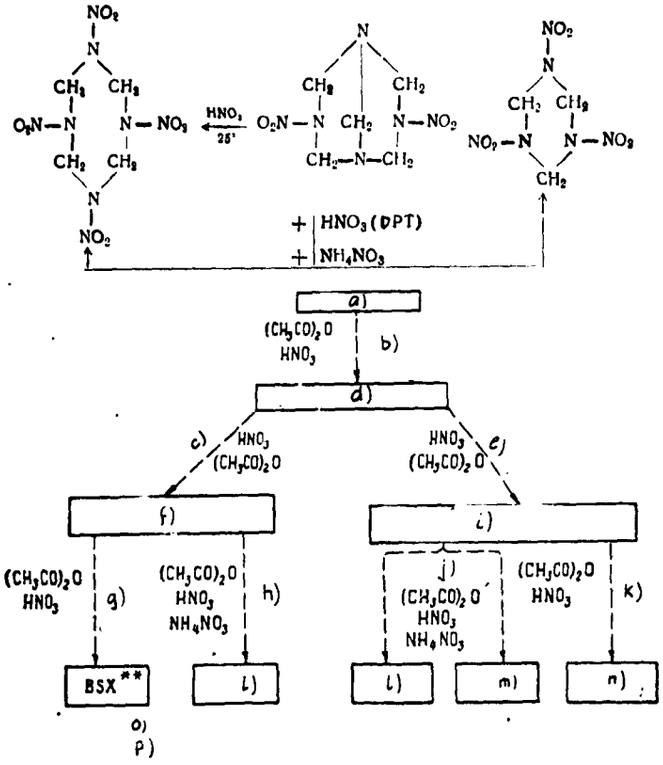


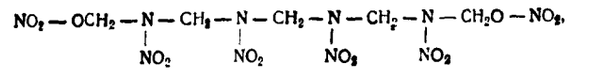
Fig.78 - Nitrolysis of Urotropine by Nitric Acid in the Presence of Ammonium Nitrate and Acetic Anhydride

(For captions, see next page)

Fig.78 (cont'd)

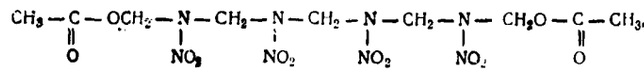
a) Urotropine; b) Stage 1 (very fast); c) Stage 2 (fast); d) By atomic compound; e) Stage 3 (fast); f) Six-term-ring compound; g) Stage 4 (slow); h) Stage 5 (slow); i) Carbon compound for oxygen and hexogen (possibly DPT*); j) Stage 6 (slow); k) Stage 7 (slow); l) Hexogen; m) Oxygen; n) Linear products; o) *Dinitropentamethylenetetramine; p) **Diacetoxytetramethylenetrinitroamine

When dinitropentamethylenetetramine is treated with nitric acid containing N_2O_5 at 0 - 25°, a linear compound 1,9-dinitrooxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane (III): is isolated:



(III)

which, under the influence of sodium acetate solution in acetic acid is converted to 1,9-diacetoxy-2,4,6-tetranitro-2,4,6,8-tetrazanonane:

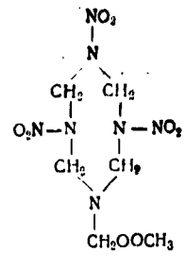


(II)

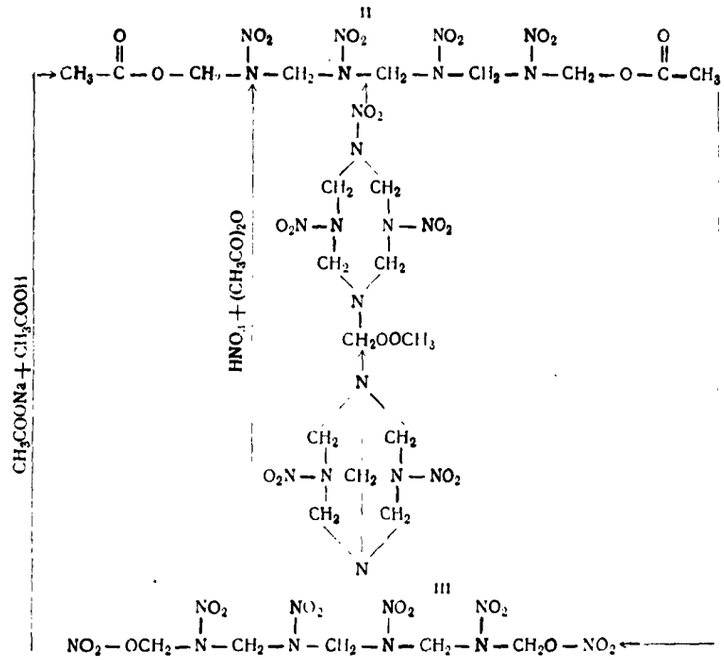
obtained earlier by Bennett and others (Bibl.77).

269 1,9-diacetoxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane may be obtained directly from dinitropentamethylenetetramine by treating it with a mixture of HNO_3 and $(CH_3CO)_2O$ at 44°. Addition of NH_4NO_3 to this system at 65 - 70° directs the reaction towards the formation of hexogen (Bibl.74).

Marcus and Winkler (Bibl.78) also obtained diacetoxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane from dinitropentamethylenetetramine through the following intermediate: 2-acetoxymethyl-4,6,8 trinitrocyclotetramethylenetetramine (PHX):



The mechanism due to McKay and others (Bibl.76) appears as follows:



Formation of oxygen in the presence of ammonium nitrate in a solution consisting of the system HNO_3 - $(CH_3CO)_2O$ means that NH_4NO_3 either facilitates the removal of formaldehyde or prevents etherification. These effects are apparently interrelated. Thus, for example, it is known that when ammonium nitrate dissolves in this mixture, the reaction temperature has to be raised

60 - 70°, before the nitric acid becomes effective for etherification, or for nitrolysis. Raising of the temperature is apparently necessary in order to clean off the formaldehyde.

270 Thus, the mechanisms of Chute (Bibl.55), McKay, Richmond, and Wright (Bibl.77), as supplemented by Marcus and Winkler (Bibl.78) support the right side of the general mechanism due to Epstein and Winkler (Bibl.75).

The literature also describes a number of the methods of producing hexogen, but these have hitherto not been practical applications.

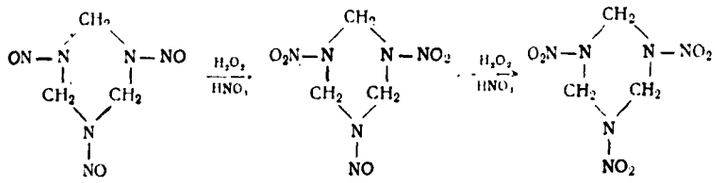
Methods (Bibl.79, 80) have been suggested for the production of hexogen that, it is claimed, yield 90% yields, based on treatment of urotropine with nitric acid in the presence of P_2O_5 according to one patent, and in the presence of acetic anhydride, ammonium nitrate, and lithium nitrate in accordance with a second patent.

One mole urotropine is added, in 25 min, at 65°, to a mixture of 4.25 moles HNO_3, 4.16 moles NH_4NO_3, 5.7 moles $(CH_3CO)_2O$ and 2.58 moles $Li(NO_3)_2$.

Caesar and Goldfrank (Bibl.81) have proposed the production of hexogen by nitration of utropine by a solution of N_2O_5 in chloroform, carbon tetrachloride, or dichloropropylene. According to the authors, nitrolysis by this method may be performed either batchwise, or continually, in either case the product yield is high.

An interesting method of preparing chemically pure hexogen was developed by Brockman and others (Bibl.82). The initial product is 1,3,5-trinitroso-1,3,5-triazacyclohexene, which is made from urotropine. The nitroso compound

reacts vigorously (with ignition) with concentrated nitric acid at low temperature. However, at a temperature of -40°, the reaction goes calmly. The authors oxidized a mixture in 82 equivalents of 99% HNO_3, three equivalents of H_2O_2 and 3.7 equivalents of H_2O (in the resultant mixture, the HNO_3 concentration is 92 - 94%). This solution was cooled to -40°, and one equivalent of nitroso compound was added to it, gradually, with vigorous agitation. The nitroso compound dissolved under these conditions. When the consequent solution was decanted onto ice, a bright yellow precipitate came down, which was 1-nitroso-3,5-dinitro-1, 3,5-triazacyclohexene. When this product was returned to the same oxidizing mixture at -40°, and the solution was allowed to heat up to 20°, it converted to chemically pure hexogen with a melting point of 204°. The product yield was about 75% of the theoretical. Thus, the reaction of conversion of 1,3,5-trinitroso- 1,3,5-triazacyclohexene to hexogen proceeds as follows:



Properties of hexogen. Hexogen consists of white odorless and tasteless crystals. As shown by the most recent investigations, it is a powerful poison (Bibl.83), and therefore safety rules must be rigorously adhered to in working with it.

The specific gravity of hexogen is 1.816, and its gravimetric density is 0.8 - 0.9 kg/ltr. Pressing at a pressure of 2000 kg/cm^2 yields a density of 1.73. The melting point is 204.5 - 205° (Bibl.82). The technical product obtained

by direct nitrolysis of urotropine by nitric acid fuses at 202°, [illegible] corresponding to approximately 1% impurities content. By boiling with nitric acid, the melting point of hexogen may be raised to 203.5°, and repeated recrystallization out of acetic acid raises the melting point to 204.5 - 205° (Bibl.82). The specific heat of hexogen at 0.30 kcal/gm°C, and the heat of crystallization is 21.3 kcal/mole (Bibl.84).

Hexogen is non-hydroscopic, and poorly soluble in water, ether, alcohol, [illegible] chloroform, and weak nitric acid. It is readily soluble in acetone and concentrated nitric acid. The solubility of hexogen [illegible] various solvents (Bibl.85,86) is presented in Tables 81 and 82.

The solubility of hexogen in boiling butyl acetate is [illegible] 7.8%.

271 Table 83 presents data on the solubility of hexogen in aniline and in mononitrotoluene, and Table 84 presents the solubility in a number of [illegible] new solvents (Bibl.87).

Table 81

a)	b)	c)
Water	15	0,01
"	100	0,15
Acetone	20	7,413
"	53	17,50
Ethyl alcohol	20	0,104
Methyl alcohol	21	0,187
Benzene	21	0,015
Toluene	18	0,032
Chloroform	20	0,008
Anhydrous ether	20	0,038
CS_2 and CCl_4	18	d)
Cyclohexane	25	12,7
"	97	27,0
Nitrobenzene	25	1,5
"	97	12,4

a) Solvent; b) Temperature, °C; c) Solubility of hexogen in 100 gm solvent, gm; d) Does not dissolve

Table 2

a)	b)
93	12,5
80	2,2
70	0,44
60	traces

a) HNO_3 concentration, %; b) Hexogen solubility, %

Table 83

a)	30	40	60	80	95	108	135	140	154
b)	0,40	—	2,55	3,65	4,20	—	4,74	—	5,12
c)	—	1,93	3,81	—	9,03	12,22	27,4	29,43	—

a) Temperature, °C; b) Solubility in aniline in %; c) Solubility in mononitrotoluene in %

Table 84

a)	b)						
	c)	d)	e)	f)	g)	h)	i)
25	1,6	2,8	2,6	3,1	1,5	1,6	31,9
100	9,3	13,3	10,0	13,5	7,9	6,4	71,1

a) Solubility of hexogen at temperature, °C; b) Solvents; c)Cellosolve; d) Methyl-cellosolve; e)Carbitol; f) Methyl-carbitol; g) Acetate-carbitol; h) Butyl-carbitol; i) Dimethylformamide

(cont'd on next page)

Annotation. Cellosolve - is glycol monoethyl ether $CH_2(OH)CH_2(OC_2H_5)$;

methyl-cellosolve - is ethylene glycol methylether $CH_2(OH)CH_2(OCH_3)$;

carbitol - is diethylene glycol ethyl ether $CH_2(OH)CH_2-O-CH_2-CH_2(OC_2H_5)$;

Methyl-carbitol is diethyleneglycol methylether $CH_2(OH)CH_2-O-CH_2-CH_2-CH_2(OCH_3)$;

acetate-carbitol is diethyleneglycol monoacetate monomethylether

$(CH_3COO) \cdot CH_2-CH_2-O-CH_2-CH_2(OCH_3)$; butyl-carbitol is diethyleneglycol butylether

$(C_4H_9O) \cdot CH_2-CH_2-O-CH_2-CH_2(OH)$.

Hexogen is crystallized out of acetone in the monoclinic system, and out of nitric acid in the tetragonal system.

Table 85 illustrates the eutectic mixtures formed by hexogen and other organic substances (Bibl.86).

Table 85

a)	b)	c)
Para-nitrotoluene	about 0,5	50,4
Para-nitroanisole	about 0,5	50,9
α-nitronaphthalene	about 1,5	55,4
Meta-dinitrobenzene	8	85
α-trinitrotoluene	2,5	78,6
1,3,5-trinitrobenzene	about 3,3	113,8
Picric acid	12	112,9
Tetryl	10	118,1
Dimethyldiphenylurea	17	112,4
Diethyldiphenylurea	3	70,4
Camphor	22	137,5

a) Organic substance; b) Quantity of hexogen in the eutectic, %;

c) Freezing point of eutectic, °C

Hexogen is stable to solar radiation.

Hexogen is a neutral substance that does not react with dilute acid. Concentrated sulfuric acid composes it in accordance with equation (Bibl.88).

$$(CH_2NNO_2)_3 + 2H_2SO_4 \rightarrow 3CH_2O + 2HNSO_5 + 2N_2 + H_2O.$$

This reaction is explained by the insignificant yield of hexogen when urotropine is nitrated with mixed sulfuric and nitric acid even containing a little H_2SO_4 (the mixed acid consists of: 88% HNO_3; 8% H_2SO_4; 4% H_2O).

Hexogen dissolves in concentrated nitric acid in the cold without decomposition and may be precipitated therefrom simply by diluting the acid with water.

When hexogen is treated with alkali dissolved in an aqueous acetone solution, hydrolysis occurs (Bibl.89). The energy of activation of this hydrolysis is equal to 14 kcal/mole (Bibl.90). The high speed of hydrolysis of hexogen by dilute caustic soda solution is employed in industry to remove hexogen from the apparatus (Bibl.60).

The hydrolytic cleavage of hexogen also occurs when it is cooked with water in an autoclave at a temperature over 150° (the technical method of removing acid from the hexogen crystals). HNO_3, CH_2O, NH_3 (as nitrate) as well as $C_6H_{12}N_4$ are found in the mother liquors (Bibl.91). The hydrolysis apparently goes in accordance with the following equation:

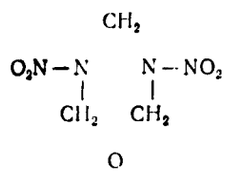
$$(CH_2NNO_2)_3 + 6H_2O \rightarrow 3H_2CO + \frac{3NH_3 + 3HNO_3}{3NH_4NO_3}.$$

Hexogen, prepared by the acetic anhydride method contains oxygen as

an impurity.

The amount of oxygen in the hexogen is determined by thermal analysis based on the melting point of the hexogen-oxygen mixture (Fig.79).(Bibl.82). The bottom line of this mechanism represents the first observed softening of specimen, whereas the upper line denotes the disappearance of the final crystal thereof.

273 Hexogen obtained by the method of nitrolysis contains bound HNO_3 and oxyhexogen (up to 0.04%). Oxyhexogen



is a white crystalline substance with melting point of 92 - 98° and crystallizes out of a mixture of water and acetone. Its solubility in acetone is greater than that of hexogen, and therefore it remains in the mother liquor. Oxyhexogen is stable in the pure form and therefore its presence in hexogen does not affect the stability of the latter (Bibl.91).

Hexogen is highly stable and may be stored for months at 50° without decomposition. It withstands the Abel test at 60° for more than 60 hrs. The stability of chemically pure hexogen considerably exceeds that of tetryl, but the stability of the technical product is not infrequently lower than this. There may be two reasons for the inadequate stability of technical hexogen.

The first is the presence in the product of diacetoxytetramethylenetrinitroamine

as an impurity (BSX). This latter may be present in hexogen obtained by the acetic anhydride method. Hexogen is stabilized by long-term boiling in water, during which the unstable diacetoxytetramethylenetrinitroamine decomposes.

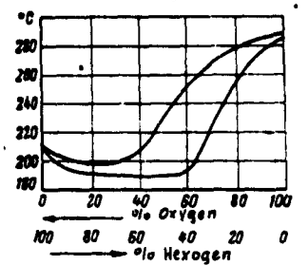


Fig.79 - Diagram of Fusibility of Hexogen-Oxygen Mixture
a) Oxygen; b) Hexogen

A second reason for the inadequate stability of technical hexogen is the presence of nitric acid therein that has not been washed out. This shortcoming is inherent in hexogen obtained by the nitrolysis method, in which the hexogen is isolated from 55% nitric acid. The hexogen crystals formed contain bound nitric acid, the removal of which occurs very slowly even upon long boiling and the presence of small crystals. In order to achieve 0.13% hexogen acidity, a long period of washing (40 - 50 hours) is required. This is difficult to achieve under industrial conditions (Bibl.91). The presence of a considerable amount of nitric acid in the technical hexogen induces corrosion and renders utilization of standard specimens difficult in determining stability. It has been shown (Bibl.91) that nitric acid virtually does not reduce the stability of hexogen. Thus, a second reason for the low stability of technical hexogen is essentially merely apparent.

The acid present in hexogen destroys the packaging material upon storage. It has been suggested that this phenomenon be combated by adding 3 - 4% N, N'-diphenylethylenediamine or some other similar substance, capable of

reacting with nitrogen oxide, to the packaging (Bibl.92).

Upon heating, hexogen starts to decompose with noticeable rapidity to 200°. The flash point is 230° (Bibl.93). In the open air, hexogen burns with a bright white flame, leaving no residue, whereas upon rapid heating it decomposes with explosion.

Pure hexogen is thermally stable.

The comparative data on stability due to Hansen (in terms of pH) after heating 5 gms of [illegible]/substance at 132° are presented in Table 86.

274 Data on the stability of mixtures containing hexogen, ammonium nitrate, and dicyandiamide, are presented in a work by Brandimarte (Bibl.94).

Table 86

a)	b)	c)	d)
0	6,53	6,85	6,56
1	—	3,11	3,03
2	5,81	2,96	2,64
3	—	—	2,32
4	—	2,89	2,22
5	5,73	—	red fumes
6	—	—	—
7	—	2,73	—
8	5,68	2,68	—

a) Heating time, hrs; b) Hexogen; c) Tetryl; [illegible] d) PETN

In stop sensitivity, hexogen occupies a position midway between tetryl and [illegible] PETN. In impact testing, a 2 kg weight causes explosion of hexogen when dropped from a height of 30 - 32 cm. Sensitivity in the standard test (p = [illegible] 10 kg, h = 25 cm) [illegible] is 80%.

explosive
The heat of [illegible] decomposition of hexogen is 1320 kcal/kg, the

explosion velocity
volume of gaseous [illegible] products is [illegible] 910 ltr/kg, the [illegible] of detonation

(φ = 1,7) 8400 m/sec, [illegible] expansion in the Trauzl block is 470 cc.

phlegmatized
The explosive [illegible] properties of [illegible] hexogen diminish substantially

with increase in the quantity of [illegible] phlegmatizer (Bibl.95).

Hexogen is employed to fill small-caliber shells, shaped charges, in

[illegible] detonators, and in caps. In a mix with aluminum powder or trotyl, [illegible] it is

employed to fill various types of munitions. Also employed are mixtures of the

[illegible] following [illegible] percentage composition:

Trotyl	60	80	20	12.5	50
Hexogen	40	20	78.5	75.0	40
Paraffin	-	-	1.5	-	-
Tetryl	-	-	-	12.5	-
Aluminum	-	-	-	-	10

Hexogen is also employed in so-called plastic high explosives or [illegible]

explosive putties. A mixture of hexogen and a binder is soft, plastic, and somewhat

blasting,
tacky. These are employed in [illegible], for example, may be used to cut metal, [illegible]

to demolish
bridge girders, blow up tanks, reinforced-concrete fire points, etc. Mixtures

of this type [illegible] consist of 88 parts finely-ground hexogen and 12 parts

78%
grease or [illegible] hexogen and 22% resinous [illegible] binder consisting of a

nitro derivative of an aromatic hydrocarbon and nitrocellulose.[illegible]

Section 2. Technology of Hexogen Production (Bibl.45, 47, 63, 86, 96, 97)

During World [illegible] War II, the production of hexogen attained particularly

large
[illegible] scope in Germany, USA, England, and Canada. In the course of the War, hexogen

production capacities increased sharply, for example, by more than 90-fold in Germany (from 600 tons in 1938 to 56,600 tons in 1944).

In Germany, a total of five methods were employed in hexogen manufacture, of which the major one was the SH method, consisting of nitrolysis of urotropine
275 with concentrated nitric acid. The other methods were experimental and actual production of hexogen by those methods was considerably lower than the capacities of the installation.

In England (Bibl.45), development of a method of hexogen production began in 1932, and in 1933 a plant producing 34 kg of hexogen per hour without recovery of the spent acid was already in operation. At the end of 1939, recovery of nitric acid wastes by absorption of nitrogen oxide and concentration of the spent acid was achieved. This made it possible to recycle about 5.5 ton of nitric acid per ton of finished product. In 1941, a plant began to function in the vicinity of Bridgewasher, producing 90 tons of hexogen per week, and subsequently this figure was doubled. Hexogen was obtained by direct nitrolysis of urotropine by concentrated nitric acid or by the so-called oxidizing method. By 1942, the acetic anhydride method, which is economically much more advantageous, was developed. In the United States and Canada, hexogen was produced by the same methods as in England. The first plant, started in the summer of 1941, worked on the basis of a technology borrowed from Britain (Bibl.69). Simultaneously, joint investigations were carried out in the USA, England, and Canada, and the development of a technology for the production of oxygen by the acetic anhydride method (Bibl.69). In February 1942, an experimental plant was put into operation

for the production of oxygen by the acetic anhydride method in continuous apparatus, and subsequently (1943), a plant went into operation at which the spent acid was completely recovered.

Production of Hexogen by the Oxidizing Method (Bibl,60)

English Variant

A technological process for the production of hexogen consists of three stages: nitration, washing, and drying, performed in separate buildings.

Nitration. At this stage, nitrolysis of urotropine is performed by direct metering of crystalline urotropine and concentrated nitric acid into a cooled reaction mixture consisting of the same ingredients. The resultant solution contains hexogen and various undesirable byproducts, as well as a considerable quantity of unutilized nitric acid.

This solution is run into a vessel in which it is diluted with water to crystallize the hexogen out. The nitro mass is held at high temperature, so as to make it possible for the byproducts dissolved therein to decompose. The residual weak acid is separated from the solid hexogen by continuous filtration and is mixed with weak acid obtained from absorption columns, before being sent to concentration.

These processes are performed in two or three nitrators and two dissolvers, arranged in series.

A nitrator (Fig.80) consists of a rectangular vessel of stainless steel divided by partitions into three sections each having an agitator. In the first section there are three concentric coils (cooling surface 1.8 m^2). The second and third compartments have one coil each. The temperature of the nitro mass in

the first and second sections must not be over 25°. In the third section of the nitrator, hot water circulates in the coil, and the temperature of the nitro mass is held at 38°, which facilitates increased hexogen yield.

Two gas tubes lead from the cover of the nitrator, and the first tube contains a cylindrical pyrex observation window for examination of the color of the gases emitted. The appearance of any considerable quantity of nitrogen oxides warns of the need for immediate dumping of the nitrator contents
276 into the emergency vat. The covers of the first and second compartments have apertures through which the urotropine is delivered. A feed apparatus for delivery of nitric acid is provided in the first compartment. A discharge aperture is provided in the wall of the third compartment.

The feed device for delivery of urotropine is installed in the compartment above the nitrators. This consists of a double receiving hopper having two horizontal screw feeds. These are actuated by gear boxes and meter the urotropine, so that the second feeder provides 1/4 as much as the first. The speeds may be regulated so that the total feed is from 57 - 170 kg per hour. The controlled flow of urotropine is sent through the floor through troughs into two the first two compartments of the nitrator, vertical worm conveyors being employed. The delivery of

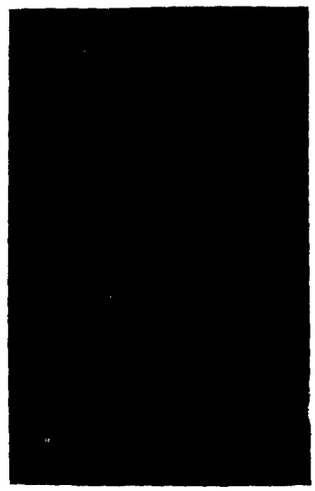


Fig.80 - Appearance of Nitrator

nitric acid into the nitrator is through a variable-area flow meter.

A discharge valve is provided in the bottom of the nitrator, through which the nitrator contents flow into a tank containing an aqueous urea solution. When the nitro mass is discharged to the solution, considerably less gas is emitted than when it is discharged into pure water. The nitro mixture goes from the nitrator into a standpipe feeding the diluter which is located somewhat lower.

The diluters (Bibl.81) are similar to the nitrators in form, but considerably larger (l = 2.6 m; b = 0.6 m; h = 1.1). The useful depth is 0.7 m. Each diluter contains four chambers for mixing, equipped with cooling coils.

The agitators have flat vanes and operate at 195 rpm.

The nitro mass emerges from the diluters through closed troughs and goes to a cooler consisting of three chambers (a principal chamber and two auxiliary chambers). The cold mass flowing from these chambers goes to classifying filters (Fig.82).

At the onset of nitration, the diluter is filled with 55% nitric acid, which is then heated approximately to 100° by steam circulating in the coils. Steam delivery is gradually diminished as the nitro mass arrives from the nitrator, and water delivery is turned on. The amount of water provided is such as to cause the concentration of the outgoing acid to be 55%. The temperature of 75° is maintained in the diluter.

The nitrogen oxides, usually liberated in the diluter, are removed from each chamber through pipes joined in a single line, which are

in turn connected to a single manifold leading to a condenser.

The nitro mass goes to the first chamber, in which water for dilution is delivered through the roof by tube. Wash water is used for this purpose. The amount of water delivered is regulated by a variable-area flow meter.

The gas line is equipped with emergency Venturi-type steam jet feed devices for use in case of a power failure or failure of the fans. The pressure depression in the gas line is held at 12 - 19 mm Hg during the entire operation. Any violation of this depression regimen may lead to filling the building with gas, as each diluter produces up to 6.8 kg NO_2 per hour under

277 normal conditions of operation. Therefore, provision is made for the use of emergency jet feeds for the gas instruments, which may be connected at the building door.

A sloping gas line runs from the building to a barometric condenser, in which the acid condensate is accumulated and from which it is returned to the system, while the non-condensing gas goes to another condenser (diameter 1.8 m, height 3.3 m, containing 706 38-mm stainless steel tubes, 2.4 m long, in three passes, cooled with water from without). The condensate is collected at the bottom and returned to the system, and the gas, which by now is cooled to 20 - 30°, proceeds along the stainless steel line leading to absorption columns (Fig.83).

The nitration building has a control panel.

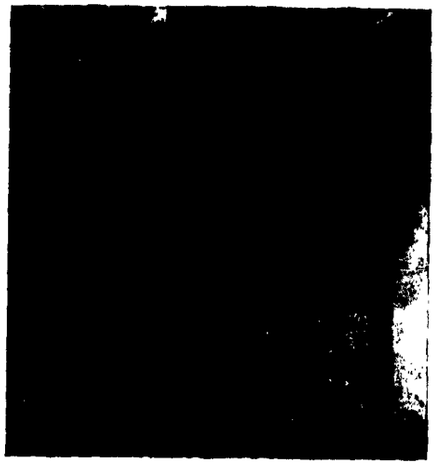


Fig.81 - Appearance of Diluter

The mass of raw hexogen and weak nitric acid go from the cooler through a closed trough to the first filter, where the spent acid is separated from the hexogen. The hexogen then goes to a second filter, in which it is washed with water to remove the remaining acid. The acid water is sucked into a sump and is later used to dilute the nitro mass.

Fig.82 - Appearance of Classifying Filter

The raw hexogen emerging from the second filter goes to a car (stainless steel) in which it is transported to the washing department. At another plant, the hexogen is washed off the filter by water into a wooden vat equipped with an agitator (500 rpm). The hexogen suspension is pumped from the vat to the washing compartment through a 50 mm tube by means of a steam-jet ejector.

Washings. Raw hexogen contains a portion consisting of coarse granular particles which have to be reduced in size inasmuch as, in the intervals between the crystals, they contain nitric acid (0.1 - 0.2%). Moreover, there is nitric

278 acid in the wash liquid remaining on the raw hexogen. The purpose of the technological processes in this stage is to reduce the size of the large hexogen grains and remove the nitric acid by washing.

A car contining raw hexogen, upon arriving at the wash building, is rolled under a steam-jet apparatus, to the suction end of which a third and a fourth hose is fastened. The water is added to the hexogen mass by means of a hose. The entire mass is picked up by the suction of a steam ejector as the hexogen softens. Thus, a single woman worker is able to empty and fill a wagon in five minutes time.

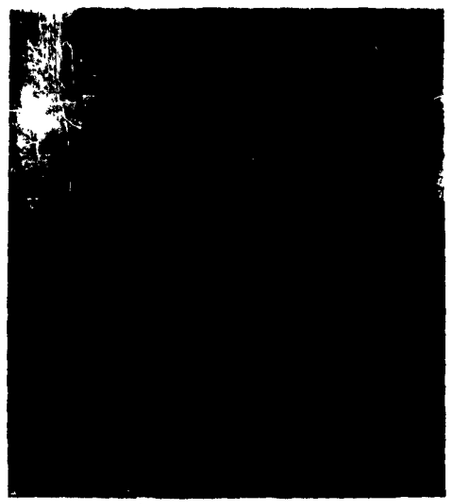


Fig.83 - Appearance of Absorption Apparatus

The suspension is ejected by steam and goes to one of the two stainless steel mixers, having a rounded bottom 1.2 m in diameter and 2.1 m high. From these receivers, the mass of water and hexogen, in approximately 3:1 ratio, goes by gravity to roller mills where the grains are crushed. Water is delivered to the rows simultaneous with the hexogen mass in order to prevent heating should delivery be interrupted. The ground mass is raised over the rollers to a 25 mm tube of stainless steel, to a height of approximately 460 mm, and may be directed into a vat by means of a rubber hose.

The vats (Fig.84) are of Columbia pine and are mounted on brick masonry piers beneath the floor. The height for each vat is 2.5 m, and its diamter 2.4 m. The bottom slopes toward the discharge aperture, over which a steel-faced valve is located. A similar valve is provided on the wall (1 m from the base) for decanting purposes. The vat has an agitator. The mass it contains is heated with live steam delivered through a bubbler, which fails by 150 mm to reach the bottom of the vat, and which ends in a slit-like nozzle.

About 2000 kg hexogen is charged into the vat. After the suspension of hexogen and water has entered the vat, the agitator is stopped, and the suspension is given 45 min to settle, subsequent to which acid water is poured into a wooden trap via a decanting valve. The mass is washed thrice with cold water, and
279 after water has been run in for a fourth washing, the mass is heated with live steam to 90 - 100° and held at that temperature for 12 hrs.

After decanting, the moist hexogen is dumped from the vat and sent for further use.

It has been suggested that, in order to obtain loose-flowing hexogen, that 0.5 - 5% potassium stearate by weight or other soluble salts of an aliphatic acid containing more than 10 carbon atoms be added to the suspension in warm water, followed by an aqueous solution of $CaCl_2$ or some other water-soluble salt (Mg, Zn, Pb, or Ni).

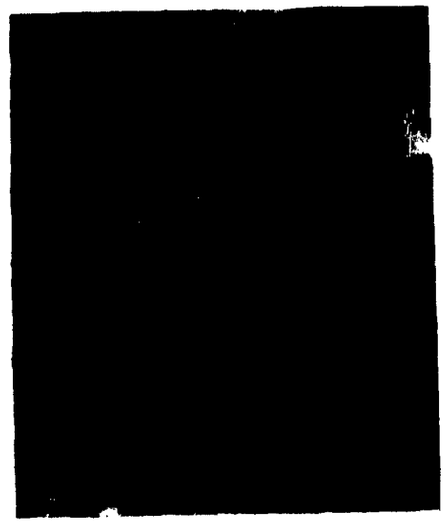


Fig.84 - External Appearance of Washing Vat

Drying. Hexogen is dried in vacuum-drying desiccators at 60°.

Hexogen to be used to make mixtures with TNT is not dried. Water removal is performed during mixing with the molten TNT.

The amount of initial products required per ton of hexogen is (in tons):

Urotropine	0.83
Nitric acid	8.78
Of which:	
Returns as spent acid (55% HNO_3)	3.48

(cont'd on next page)

Is cracked by absorption system 3.43

Goes to nitrolysis 1.87

H_2SO_4 consumed in concentration of the spent and adsorbed acid 0.49

Consequently, the hexogen yield is 37.7% in terms of formaldehyde, 56.7% in terms of the amino groups, and 9.7% in terms of nitric acid. The concentration of the nitric acid employed is 95 - 96%, and the modulus is 10.5.

280 The German Variant

The "SH" method was developed in 1937 by Schnurre (Bibl.49, 65, 86, 98).

As distinct from the English variant, the process is run in batch-type apparatus and a smaller amount of nitric acid, but of higher concentration (99% HNO_3), is employed for urotropine nitrolysis. Figure 85 presents a diagram of the technological process for the production of hexogen.

Nitric acid cooled to 0° is charged into nitrator (2), and pre-desiccated urotropine is slowly added thereto, the temperature being held at not more than 20°. To avoid liquifaction of the urotropine, it is recommended that it be charged in the form of compressed balls (Bibl.98). After nitration has ended, the nitrator contents are emitted into the buffer apparatus, from which the nitro mass passes successively through apparatus (4), (5), (6), (7), and (8), in which the urotropine undergoes complete nitration. A temperature of 15 - 20° is maintained in buffer apparatus (3) through (8). Further, the nitro mass goes from buffer apparatus (8) to stabilization in two oxidizers (principal oxidizer 9 and buffer oxidizer 10), to which water is delivered simultaneously for dilution. A temperature of 70 - 80° is maintained in the oxidizer.

Then, the suspension of hexogen in spent acid flows to the cooler (11) and then goes in sequence through three more coolers (12), (13), (14). Natural cooling takes place in the first XX three coolers, while in the last the nitro mass is cooled by water to 20°.

From cooler (14) the nitro mass is discharged into a drum filter (or centrifuge) 15, the spent acid is drained into a receiver (16), and the hexogen is washed two or three times with cold water, and then stirred with water in a mixer (17). In the mixer, the hexogen is mixed with water and the suspension is sent by centrifugal pump to autoclaves (18) (the pressure in the autoclaves is 2.5 - 3 atm) in another building, where it is heated to 130 - 140° and held at that temperature for 4 - 5 hrs.

The rate of removal of acid when hexogen is washed in the autoclave rises with increasing temperature up to 150°, but remains virtually constant thereafter. The velocity does not depend upon the relationship between the amount of water and hexogen (as it does in cooking without an autoclave), but is dependent on crystal size XXXXXX and is determined primarily by the rate of diffusion of the acid to the surface of the crystals.

281 When hexogen is washed in an autoclave, hydrolysis of the hexogen may set in at as low as 140°, and it will reach 0.5% within two hours. When the temperature is raised to 150°, the rate of hydrolysis rises sharply. The decomposition of hexogen upon washing proceeds by complete destruction of the XXXX molecule to form liquids and gases which do not impair the properties

XXX

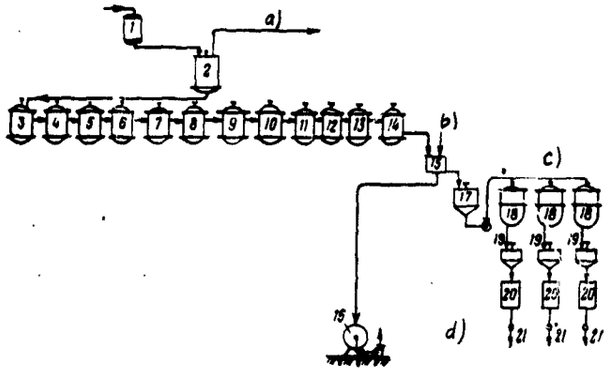


Fig.85 - Diagram of Production of Hexogen by Oxidation Method

1 - Tank for cooling HNO_3; 2 - Nitrator; 3 to 8 - Buffer apparatus to complete nitration; 9, 10 - Apparatus for oxidation; 11 to 14 - Coolers; 15 - Centrifuge; 16 - Receiver; 17 - Mixer; 18 - Autoclaves; 19 - Rectification apparatus; 20 - Filter hoppers; 21 - Sacks

a) Urotropine; b) Water; c) Cooking phase, under pressure; d) Spent acid to concentration

281 of the hexogen: the hexogen is not contuminated by its own decomposition products. (Bibl.91).

Upon conclusion of the cooking in the autoclave, the mass is cooled to 100°, and drained into a phlegmatization apparatus (19), containing fused synthetic wax colored by Sudan dye. The amount of wax used is such as to cause it to constitute 5% of the hexogen. After the hexogen suspension has been run into the wax, the mass is rapidly cooled to 20° in 30 min and drained to filter-hopper (20), where the hexogen is squeezed out to 10% moisture content within two hours. The dried hexogen is emptied into silk sacks and sent to another plant for drying.

The acidity of hexogen after washing on the filter is 0.3 - 0.4%, and after cooking in the autoclave it is 0.1%. The melting point of the resultant hexogen is 202°. 0.83 - 0.84 ton Urotropine and 7.1 ton (99%) nitric acid is consumed per ton of hexogen, of which 5.2 tons are recovered.

The oxidizing method of producing hexogen, yielding a high-quality product, is quite simple, dependable, and sufficiently safe, [illegible] has a number of significant inadequacies. The major ones are the large consumption of concentrated nitric acid and the low yield of hexogen in terms of formaldehyde (35 - 40% of the theoretical). The need for twice diluting the acid with water in order to remove the hexogen also greatly increases the cost of concentrating the spent acid or recycling. Bearing these shortcomings in mind, the researchers in a number of countries conducted investigations with the object of developing more perfect methods of obtaining hexogen. In Germany, during World War II, hexogen was obtained by other methods as well: the "acetic anhydride" ("KA"), the "white salt" ("W"), the method based on condensation of formaldehyde with ammonium nitrate in the presence of BF_3 ("E").

In the United States, England, and Canada, hexogen was obtained by the acetic anhydride method which proved considerably more effective than the oxidizing method (Bibl.69).

Producing Hexogen by the "W" Method (Bibl.63, 86)

During World War II, experimental installation operated in Germany at which hexogen was produced by the highly original "W" method (the sulfaminic acid as intermediate). A schematic diagram of this installation is presented in Fig.86.

Reaction of ammonia with sulfuric anhydride, which is metered in a ratio of 1:3, is performed in the condenser (1). This results in the formation of ammonium imino sulfonate and imino disulfonate:

$$SO_3 + 2NH_3 \rightarrow NH_2SO_3NH_4;$$
$$2SO_3 + 3NH_3 \rightarrow NH(SO_3NH_4)_2.$$

The salt obtained is dissolved in thrice the amount of water and discharged into vats (2), whereupon calcium oxide is added, in 110% of the theoretically necessary quantity. The solution is heated by live steam to remove the ammonia, and it is filtered free of the excess calcium hydroxide on filter (3). The filtrate is received in vat (4), where it is acidified with sulfuric acid from metering tank (5). In these operations, the following reactions occur:

$$NH_2SO_3NH_4 + NH(SO_3NH_4)_2 + 2Ca(OH)_2 \rightarrow$$
$$\rightarrow (NH_2SO_3)_2Ca + CaSO_4 + 3NH_4OH.$$

282 When calcium iminosulfonate is acidified, it hydrolyses to form sulfaminic acid.

In order to produce potassium sulfaminate, potassium oxide and potassium bisulfate are run into vat (4) after acidification and agitation:

$$NH_2SO_3H + KHSO_4 + Ca(OH)_2 \rightarrow NH_2SO_3K + CaSO_4 + 2H_2O.$$

Then, the potassium sulfaminate is filtered on funnel (6) free of the $CaSO_4$. The filtrate then goes to a vacuum evaporating column (7), where it is vaporized, and then goes to crystalliser (8) and filter (9). The filtered crystals of

potassium sulfaminate go to condenser (10), into which formalin is added from vat (11). A condensation reaction is run at 30°, the pH of the solution being held at 5. The solution is then steamed in the vacuum vaporizing apparatus (12), cooled in crystallizer (13), and the crystals are filtered off on hopper (14). The potassium cyclotrimethyleneiminosulfonate ("white salt") obtained is dried in desiccator (15).

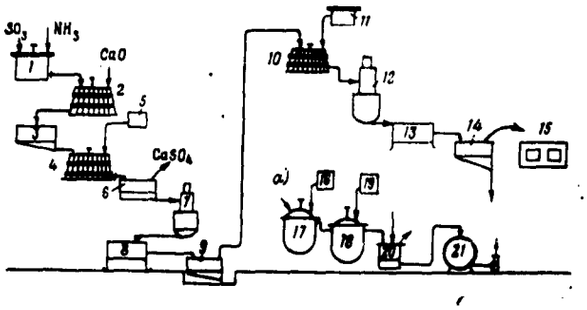


Fig.86 - Diagram of Production of Hexogen via Sulfaminic Acid

1 and 10 - Condensators; 2 and 4 - Vats for decomposition; 3, 6, 9, 14, and 20 - Filter hoppers; 7 and 12 - Evaporation columns; 8 and 13 - Crystallizers; 5, 11, 16, and 19 - Metering tanks; 15 - Dryer; 17 - Nitrator; 18 - Diluter; 21 - Receiver

a) "White salt"

The nitration of "white salt" is performed by a nitro mixture of the following composition: 80 - 81% HNO_3; 4 - 5% H_2SO_4; 13 - 14% SO_3, and 1 - 2% N_2O_4, which is delivered from metering tank (16) (the quantity being 1.8 parts by weight per 1 part "white salt") into nitrator (17). The nitro mass goes from nitrator (17) to diluter (18), into which water is delivered from metering tank (19) for dilution to a specific gravity of 1.2 - 1.3. Then the hexogen is

filtered [illegible] free of the spent acid on filter (20), and, after first being washed with water, goes to the final washing and stabilization. The spent acid is of the following composition: 23% HNO_3; 13 - 14% [illegible] H_2SO_4; 10 - 11% $KHSO_4$; 52 - 54% H_2O.

Production of Hexogen by Method "K" (Bibl.63, 86)

In 1936, Knoffler developed a method of producing hexogen called method "K". Figure 87 presents a schematic diagram of the technology involved in the production of hexogen by [illegible] this method.

283 Urotropine is nitrated by a solution of ammonium nitrate in concentrated nitric acid. Nitration is performed in two stages. In the first stage, urotropine is added to a solution of ammonium nitrate in nitric acid at 20°. This results in the formation of hexogen and formaldehyde. The latter reacts, in the second stage, at a temperature of 65 - 70°, with ammonium nitrate and nitric acid, to form additional hexogen. The mass is then cooled.

The hexogen obtained is separated from the spent acid on a drum filter, washed with water, and crystallized out of acetone. If necessary, the hexogen is subjected to phlegmatization.

The spent acid contains a certain amount of formaldehyde, as a consequence of which it is unstable and cannot be [illegible] subjected to regeneration. Therefore, the spent acid is first heated in special apparatus 90 - 95°. This is accompanied by complete oxidation of formaldehyde and partial decomposition of ammonium nitrate. The nitrogen oxides and nitric acid vapors liberated therein

[illegible]

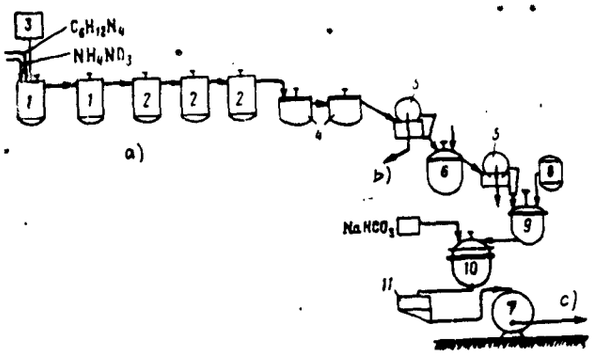


Fig.87 - Diagram of Production of Hexogen by Method "K"

1 - First-stage nitrators; 2 - Second-stage nitrators; 3 - Metering tank for nitric acid; 4 - Coolers; 5 - Drum-type vacuum filters; 6 - Washing apparatus; 7 - Acetone collector; 8 - Acetone metering tank; 9 - Dissolver; 10 - Crystallizer; 11 - Filter-hopper

a) Nitration; b) Spent acid; c) Acetone to purification

go to an absorption apparatus. The stabilized nitric acid, containing about 48% HNO_3 and 24% NH_4NO_3 are subjected to distillation in a special apparatus.

The major advantage of the "K" method is a good yield of hexogen (60% of theoretical in terms of formaldehyde). Serious shortcomings of the method are: the large amount of material that have to be processed (more than 14 tons of product per tons of hexogen, which results in a pronounced reduction of the productivity of the apparatus, and complicates the process), and the very complex process of recovery of the nitric acid and ammonium nitrate.

0.48 - 0.5 ton Urotropine, 4.8 tons ammonium nitrate, and 8.6 tons nitric acid are consumed per ton of hexogen. 3.6 tons Ammonium nitrate, and 7.2 tons nitric acid are recovered.

284 Production of Hexogen by the Acetic Anhydride Method

German Variant (Bibl.63, 86)

In Germany, two methods of producing hexogen with the use of acetic anhydride have been developed: the "KA" and "E" method.

The "KA" method is a further improvement of the "K" method. The technological process of production by the "KA" method consists of the following operation: 1) making urotropine dinitrate; 2) making ammonium trinitrate; 3) nitrolysis of urotropine dinitrate by ammonium trinitrate in the presence of acetic anhydride at 50 - 60°; 4) filtration of the hexogen free of acids, washing of the hexogen, and stabilization thereof by cooking with water under pressure; 5) drying of the hexogen; 6) regeneration of acetic anhydride and spent acid.

First the dilute spent acid is regenerated by decomposition at 700°. This is [illegible] accompanied by conversion of the acetic acid into monomolecular anhydride-ketene:

$$CH_3COOH \rightarrow CH_2=CO+H_2O.$$

Ketene is a gas that reacts with acetic acid to form acetic anhydride:

$$CH_2=CO+CH_3COOH \rightarrow (CH_3CO)_2O.$$

The hexogen yield by this method [illegible] attains 75 - 80% of the theoretical in terms of formaldehyde. Shortcomings of the method include production of hexogen of low melting point (not over 192°) and the danger involved in the recovery of spent acetic acid, inasmuch as it contains unstable products.

The products consumed per ton of hexogen are 1.4 ton urotropine, 0.43 ton ammonium nitrate, 0.68 ton (99%) nitric acid, and 2.4 ton acetic anhydride.

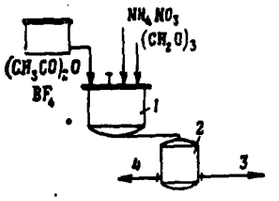


Fig.88 - Diagram of Production of Hexogen by the "E" Method
1 - Reactor; 2 - Nutsch; 3 - Hexogen to washing; 4 - Mother filtrate (to separation of catalyst)

Another method of producing hexogen was developed in 1935 - 1938 by Elbe, and was termed method "E". The initial products are paraformaldehyde, ammonium nitrate, acetic anhydride, and boron fluoride as promoter. Figure 88 illustrates the schematic diagram for the production of hexogen by this method. The process is carried out as follows.

Paraformaldehyde and dry ammonium nitrate are introduced into the acetic anhydride containing boron fluoride (0.4% BF_3) and heated to 60 - 65°. The hexogen produced is separated from the spent acid on a suction filter. Nutsch. The spent acetic acid is distilled and again converted to acetic anhydride, which is recycled.

Advantages of the method include the high yield of hexogen (80% of theoretical, computed in terms of formaldehyde) and the use, as the nitrating substance, of ammonium nitrate, which is cheaper than concentrated nitric acid. Shortcomings are the low melting point of the hexogen obtained, as a consequence of the fact that it contains impurities (about 7%), and the danger involved in recovering the spent acid. Other difficulties include the complexity of preparation of paraformaldehyde, and the large consumption of ammonium nitrate and acetic anhydride.

The following is the consumption per ton of hexogen: 0.63 - 0.635 ton paraformaldehyde, 1.8 ton ammonium nitrate, 5 - 5.1 ton acetic anhydride, and 0.019 ton boron fluoride. The hexogen obtained contains up to 6% oxygen.

285 The Canadian Variant (Bibl.45, 69, 96)

In Canada, the United States, and England, work was done jointly in the development of an acetic anhydride method of producing hexogen (Bibl.69). In October 1940, Ross and Shisler (Bibl.72) observed that reaction of formaldehyde and ammonium nitrate with acetic anhydride yields hexogen:

$$3CH_2O + 3NH_4NO_3 + 6(CH_3CO)_2O \rightarrow (CH_2NNO_2)_3 + 12CH_3COOH.$$

This reaction does not require the use of urotropine or large amounts of nitric acid. The new method employs acetic anhydride, which these countries were in a position to produce in large quantities (Bibl.69).

The investigations were begun in Canada by a group working under the leadership of Bachman of Michigan University, and were tested at Canadian plants. Bachman's work showed that Ross' reaction could be combined with a nitrolysis reaction so as to get the best results. Inasmuch as the initial products of the Ross reaction - formaldehyde and ammonium nitrate - come into being as waste of the nitrolysis reaction, further addition of ammonium nitrate and acetic acid to the nitro mass had to result in the formation of an added molecule of hexogen. This was confirmed by experiment.

The equation for the combined process suggested by Bachman (Bibl.67, 68) may be depicted as follows:

$$C_6H_{12}N_4 + 4HNO_3 + 2NH_4NO_3 + 6(CH_3CO)_2O \rightarrow$$
$$\rightarrow 2(CH_2NNO_2)_3 + 12CH_3COOH.$$

In February 1942, a DuPont Plant began operations to produce hexogen under this combined method. In May 1942, production of hexogen by the combined method was begun at an Eastman Plant. At this plant, the process was performed in continuous apparatus, and the spent acid was recovered in acetic anhydride, and then again employed to produce hexogen. // The acetic anhydride method of producing hexogen, which resulted in twice the yield of the nitrolysis process, proved considerably more economical for England, Canada, and the USA (which had adequate supplies of acetic acid and acetic anhydride) (Bibl.69).

The technological process for the production of hexogen by the Bachman-Ross method is as follows.

First, solutions of urotropine in glacial acetic acid and of ammonium nitrate in 97% nitric acid are prepared. The solutions are heated to 40°, and the acetic anhydride is simultaneously heated to 60°. The prepared solutions are slowly run into the acetic anhydride. Run-in of the components is performed at 70 - 75°. Upon completion of run-in, the mixture is held for 15 - 20 min at the same temperature, and then 640 moles of water heated to 40° is added to the nitro mass (Bibl.45).

The generation of the acetic acid is performed by adding sulfuric acid to the spent acid in two processes. The first portion consists of 5 - 10% of the weight of the spent acid, whereupon the mass is heated to 100°. The second portion is 15 - 40%. The mixture is subjected to distillation at 120 - 140° for the purpose of driving off the acetic acid (Bibl.99). It is recommended that the spent acid

first be treated with NH_3 in order to reduce the HNO_3 content to 1% (Bibl.100). It is suggested that the nitro mass obtained be diluted with water at 90 - 100°, and that after separation of the hexogen, it be subjected to distillation to drive off the acetic acid (Bibl.101).

Safety Procedure in Hexogen Manufacture

In addition to the safety rules common to the production of all explosives, the high sensitivity of hexogen to mechanical effects must be borne in mind. All hexogen shops are dangerous in terms of explosion and fire, except
286 for the urotropine production shop, where the only danger is that of fire.

The harmful physiological effects of hexogen dust, urotropine dust, as well as of nitrogen oxides and nitric acid must be noted.

Buildings in which hexogen are produced, and the apparatus in which the process occurs have to be provided with the appropriate devices to assure safe operation.

In England (Bibl.60), the production of hexogen is carried out in a number of small buildings separated by substantial distances. All the buildings are surrounded by embankments and connected by special corridors open to the side. The roofs of these corridors are of asbestos cement and serve solely for protection against rain. The floors both of the buildings and of the corridors are of asphalt. The walls are cement. The buildings have lightening rods, and the apparatus is provided with special equipment to remove static electricity.

In work in the shop, blows of metal against metal are wholly ruled out. Particular attention is directed at the cleaning of the plant before repair. Solidified explosive is cleaned only with wooden equipment, the cleaning is performed very carefully, and is observed by a technologist. When units have to be heated or repaired by welding, a technologist checks them out by test burning. To do this, small one-man steel shelters, with apertures for the hands, and viewing slits were employed. The burner has a handle 1.8 m long.

Although it contains some acid or water, hexogen in the various stages of production is none the less highly sensitive to mechanical effects.

However, the major measure for prevention of fires and, particularly, of explosions, in hexogen production, is strict adherence to the technological procedures.

In the nitrolysis process, exothermic reactions occur in the stage of nitration. Even when the violation of the technical process is comparatively minor, these reactions readily lead to ejection of the nitro mass from the apparatus, or flare-up. It is at this stage that concentrated nitric acid is employed, contact of which with urotropine or with foreign organic substances in the absence of agitation readily induces a vigorous reaction and ignition.

In production, urotropine may catch fire in the charging hopper or on the feed conveyor under the influence of nitric acid fumes or spatter. Therefore, careful observation of the condition of these portions of the apparatus, and periodic cleaning thereof is essential.

It must be borne in mind that accidents may occur, in the process of stabilization of the spent acid, not only at very high, but also at low reaction temperature. At low temperature (40 - 45°), the oxidation process goes considerably more slowly, as a consequence of which unoxidized impurities accumulate in the nitro mass. This may give rise to a vigorous reaction with ejection of the nitro mass. The degree of dilution of the nitro mass by water has the same effect upon the oxidation process.

Taking the foregoing into consideration, it is necessary carefully to monitor the hexogen production process. Moreover, the most reliable type of monitoring, guaranteeing the safety of the process, is automatic monitoring with automatic regulation of the process.

When hexogen is produced by the acetic anhydride method, the following has to be borne in mind.

Acetic anhydride and acetic acid may form explosive mixtures when mixed with nitric acid or ammonium nitrate solution in nitric acid in particular ratios. A mixture with a zero oxygen balance may be obtained when one part acetic anhydride by weight is mixed with two parts nitric acid. The greater the amount of nitric acid in the mixture, the more dangerous the mixture will be (Bibl.99). Mixtures containing 20 parts acetic anhydride by weight per part nitric acid by weight are deemed to be safe in terms of explosion.

287 When hexogen is obtained by this method, the nitric acid content in the nitration mass is only 3%, whereas the acetic anhydride content may be up to 7%, and acetic acid up to 85%. Consequently, from the viewpoint of formation

of explosive mixtures, the reaction mass is sufficiently safe. Danger may arise only if very extreme deviation from the metering occurs, when the anhydride and nitric acid ratios reach dangerous limits. The possibility of this kind of violation has to be ruled out by automatic metering and automatic monitoring. In this connection, the storage for nitric acid and the solution of ammonium nitrate in nitric acid should be set up in a separate building, isolated from the building where the anhydride, acetic acid, and spent acid are stored, so as to rule out the possibility that these components may come into contact.

Transportation of the acetic anhydride and acetic acid, nitric acid, and solution of ammonium nitrate in nitric acid must be separate, so as to eliminate the possibility of mixture of these components, which might result in fires and explosions.

In the building itself, the metering tanks and devices must be arranged so that the components capable of reacting with each other are unable to come into contact outside the reactor.

When the equipment is stopped without emptying the apparatus, it is necessary to eliminate the possibility of accidental entry of nitric acid or the ammonium nitrate in nitric acid solution into the apparatus by virtue of wrong functioning of the locking equipment for incomplete closing thereof.

When the work is in progress, it must be borne in mind that acetic anhydride and acetic acid fall into Class II of readily-flammable liquids. Their parameters are indicated in Table 87.

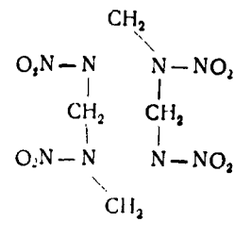
Table 87

a)	b)	c)
Acetic anhydride	43—45	385
Acetic acid	40	566
Benzene	−12+10	490
Acetone	−18+2	500
Dichloroethane	14+21	413

a) Component; b) Flash point, °C; c) Temperature of spontaneous combustion, °C

Section 3. Hexogen Analogs

Cyclotetramethylenetetranitroamine (octogen)



apparently is not yet in use at the present time, inasmuch as both its chemical properties and, even more so, its explosive properties approximate those of hexogen very closely, while the cost of manufacture is substantially higher.

288 Octogen may be obtained from the same raw materials as hexogen, but the yield is lower (Bibl.55,76,102).

Octogen is of interest as a possible admixture to hexogen (up to 10%) obtained by the acetic anhydride method. Therefore, it is necessary to know its properties, as well as the conditions of its formation, when it is undertaken to produce hexogen. This is particularly important in terms of safety procedures, inasmuch as octogen has four polymorphic forms, of which only one, the β-form, is stable. The

288 need to remove the unstable and more sensitive isomers of octogen creates further difficulties in the purification of hexogen produced by the acetic anhydride method.

Octogen is a solid crystalline light product. When slowly crystallized out of acetone, octogen is obtained in the form of large transparent crystals of rhombic shape. The product purified by recrystallization from acetone has a melting point of 276 - 277° (decomposes upon fusion). Table 88 presents some of the properties of octogen.

Table 88

Property	Polymorphic Form of Octogen			
	α	β	γ	δ
Specific gravity	1.96	1.87	1.82	1.77
Relative sensitivity to shock (180 in the case of hexogen)*	60	325	45	75
Stability (at room temperature)	Metastable	Stable	Metastable	Labile

*The higher the value, the lower the sensitivity.

Octogen is not soluble in methyl or ethyl alcohols, in benzene, toluene, xylene, or ethyl ether. It is poorly soluble in dichloroethane, aniline, nitrobenzene, and dioxane. Its solubility in water at 15 - 20° is about 0.003% and at 100° about 0.02%. The solubility of octogen in various solvents is illustrated in Table 89

Table 89

Temperature, °C	Solubility of Octogen, %			
	Acetone	Butylacetate	Aniline	Mononitro-toluene
22	2,10	1,14	—	—
27	2,65	—	0,35	—
37	3,52	—	—	—
44	4,0	3,38	—	0,89
56	4,13	—	0,49	1,23
60	—	0,57	—	—
68	—	—	0,67	—
78	—	—	0,89	—
83	—	—	1,05	—
90	—	—	1,19	—
99	—	—	1,38	—
104	—	0,77	1,61	1,60
122	—	0,88	2,09	1,98

The curve of solubility of octogen in acetone is shown in Fig.89.

289 When octogen is processed with a solution of alkali in aqueous acetone solution, hydrolysis occurs at a rate less than the rate of hexogen hydrolysis (the activation energy of the hydrolysis of hexogen is 14 kcal/mole, and that of octogen is 25 kcal/mole). This difference in the rates of hydrolysis has been employed (Bibl.90) for analysis of the octogen content of hexogen. The accuracy of determination is within ±0.2%, thanks to the process sequence. Water, 1% solutions of nitric or sulfuric acids virtually do not decompose octogen when boiled for 6 hrs. Light does not affect the octogen.

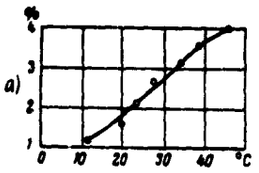


Fig.89 - Solubility of Octogen and Acetone

a) Octogen dissolved

The stability of octogen is the same as that of hexogen. A manometric specimen of octogen run for 5 hrs at 166 - 167° shows a rise of 32 - 39 mm in pressure, while that of hexogen shows a rise of 39 - 40 mm.

Table 90 shows the explosive properties of octogen when XX compared with those of hexogen. It follows from the data presented that there is virtually no difference between octogen and hexogen in terms of explosive properties.

Table 90

Property	Hexogen Obtained by the		Octogen
	Oxidizing Method	Acetic Anhydride Method	
Brisance due to Kast when Δ = 1.52, mm	4.5	4.3	5.2
Expansion in lead bomb, cc	440	481	486
Shock sensitivity at p = 10 kg and h = 250 mm, in % complete explosions	96	84	84
Flash point, °C	275	-	2991

289 In studying the mechanism of hexogen formation reactions by the acetic anhydride method (Bibl.75, 76) octogen was obtained, and the conditions of its formation were determined. Epstein and Winkler (Bibl.76) succeeded in getting a 40% yield of octogen (in terms of urotropine) when they treated urotropine with a mixture of nitric acid and acetic acid, and ammonium nitrate.

The process is performed by preliminary mixing of the prepared solutions of urotropine in acetic acid and ammonium nitrate and nitric acid with acetic anhydride, with the following molar relationship among the components

$$C_6H_{12}N_4 : NH_4NO_3 : HNO_3 : (CH_3CO)_2O = 1 : 2 : 4 : 7.$$

The yield of octogen is 40% in terms of methylene groups. The reaction apparently goes in accordance with the following equation:

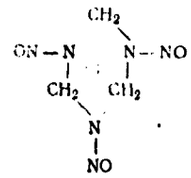
$$2(CH_2)_6N_4 \cdot 2CH_3COOH + 4NH_4NO_3 \cdot 2HNO_3 + 12(CH_3CO)_2O \rightarrow$$
$$\rightarrow 2(CH_2NNO_2)_4 + 28CH_3COOH.$$

McKay, Richmond and Wright (Bibl.76) obtained octogen by treating dinitropentamethylenetetramine with concentrated nitric acid at 10°. These studies have been set forth in greater detail in Sections 1 and 2.

Bachman (Bibl.74) developed a method of producing octogen by the action of a mixture of strong nitric acid (2.2 parts), glacial acetic acid, and acetic anhydride
290 (6.5 parts) at 15 - 30° upon urotropine. Under these conditions, about 20% dinitropentamethylenetetramine is obtained. Nitrolysis of this product at 60 - 65° by nitric acid in the presence of ammonium nitrate, and nitrogen anhydride results in the formation of octogen, with a yield of about 80% in terms of the dinitropentamethylenetetramine.

Cyclotrimethylenetrinitrosoamine (Bibl.63, 103, 104) is a homolog of hexogen.

290 It was first obtained in 1888 by Meyer by rapid mixing of a concentrated solution of sodium nitrite with an aqueous urotropine solution containing excess (computed against the nitrite) hydrochloric acid (Bibl.103), performed at low temperature. His formula is:



The product may be obtained easily by rapidly running an aqueous hexamethylenetetramine solution into an aqueous sodium nitrite solution (5 moles $NaNO_2$ per 1 mole $C_6H_{12}N_4$) and weak nitric acid, in which case the temperature has to be low (0 - 5°), and the pH of the medium has to equal unity (Bibl.49). A reduction of the acidity of the medium shifts the reaction in the direction of formation of dinitrosopentamethylenetetramine. The initial products may also be formaldehyde and ammonia (Bibl.103). When sodium nitrite is added to an aqueous solution of formaldehyde and ammonia, cyclotrimethylenetrinitrosoamine comes down virtually quantitatively (Bibl.105).

Cyclotrimethylenetrinitrosoamine is a yellow crystalline substance melting at 105°. Its solubility at 15° in 100 gm acetone is 33.4 gm, whereas in methylalcohol it is 2.35 gm, and in acetic acid (100%), it is 5.3 gm. Mineral acids decompose cyclotrimethylenetrinitrosoamine even in the cold, while pure acetic acid does not induce decomposition even when heated to 100°. The product is very sensitive to the effects of light (particularly the ultraviolet portion thereof), which sharply reduces its stability (Bibl.103). The reduced stability is also due to the presence

290 of impurities: nitrous acid and dinitrosopentamethylenetetramine.

Cyclotrimethylenetrinitrosoamine has been proposed by the German Vazag Co. as an explosive the production of which does not require strong nitric acid. However, its comparatively low chemical stability has been an obstacle to its introduction (Bibl.106). Stability may be increased by recrystallization from methyl alcohol or acetone (Bibl.103).

In its explosive characteristics, cyclotrimethylenetrinitrosoamine approximates TNT, as is evident from Table 91.

Table 91

Property	Cyclotrimethylene-trinitrosoamine	Hexogen	TNT
Melting point, °C	105	203	81—82
Density, gm/cm³	1,53	1,65	1,60
Velocity of detonation, m/sec	7500—7800	8300	6850
Brisance, in mm	4,7	5,9	4,2
Fugacity, in cc	386	489	309
Volume of gaseous products, in ltr/kg	853	853	685
Heat of explosion, in kcal/kg	900	1326	1085
Shock Sensitivity: 10 kg weight does not induce explosion when dropped from an elevation of, in cm	24	16	24

Trimethylenetrinitrosoamine is an expensive and rather powerful brisant explosive of low sensitivity to shock. A shortcoming is the low chemical stability.

291 Brockman and Downing (Bibl.82, 107) obtained chemically pure hexogen by treating this product with concentrated nitric acid, and on the basis thereof, have developed a method for producing hexogen free of impurities.

C. Nitroamines of the Aliphatic Series

Section 1. Ethylene-NN'-dinitroamine (EDNA)

Ethylene-NN'-dinitroamine (EDNA or Haleite) was obtained in 1888 by the nitration

291 of ethylene urea by mixed sulfuric and nitric acid (Bibl.108). The formula is

$$\begin{array}{l} CH_2-NH-NO_2 \\ | \\ CH_2-NH-NO_2. \end{array}$$

During World War II, methods of producing this substance, termed Haleite was studied, and in 1943, industrial-scale production began. Haleite was employed for the same purposes as tetryl. Its advantage over tetryl is higher explosive properties and synthetic raw materials. Moreover, according to American data (Bibl.109), the cost of production of Haleite is considerably lower than that of tetryl.

Ethylene-NN'-dinitramine consists of white crystals of rhombic shape. Its specific gravity is 1.75, and its melting point 175 - 176°. It is not hygroscopic, is soluble in nitrobenzene, dioxane, alcohol, and boiling water, but insoluble in ether. Solubility at various temperatures in water and ethyl alcohol are illustrated in Table 92.

Table 92

a)	b)	
	c)	d)
25	0,3	1,25
50	1,25	3,45
75	4,95	10,1
95	16,4	—

a) Temperature, °C; b) Solubility, gm of ethylene-NN'-dinitramine (in 100 gm solvent); c) Water; d) Ethyl alcohol 95%

Ethylene-NN'-dinitramine has acid properties and can produce salts with potassium, silver, and tin. The silver and tin salts are very sensitive to mechanical action.

In alkaline solution, ethylene-NN'-dinitramine is a stable compound, but in neutral and acid medium it decomposes to form ethylene glycol, acetaldehyde, and nitrous oxide:

$$2\begin{array}{l} CH_2-NHNO_2 \\ | \\ CH_2-NHNO_2 \end{array} \xrightarrow{-2N_2O} 2\begin{array}{l} CH_2OH \\ | \\ CH_2NH\cdot NO_2 \end{array} \xrightarrow{-2N_2O} \begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} + \begin{array}{l} O \\ // \\ C-H \\ | \\ CH_3 \end{array} + H_2O.$$

291 Decomposition is accelerated with rise in temperature and strength of acid.

The dry product virtually does not decompose, but the moist product starts to decompose at temperatures in excess of 50°. The decomposition products, as well as the impurities, catalytically accelerate decomposition.

The explosive properties of ethylene-NN'-dinitramine are as follows (Bibl.110, 111): flash point 180°, heat of explosion 1276 kcal/kg, volume of gaseous explosion products 908 ltr/kg, velocity of detonation 7750 m/sec (at a density equal to 1.55).

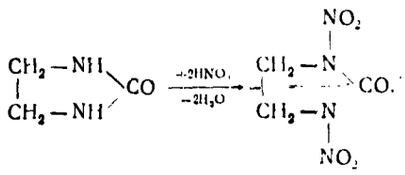
Production of ethylene-NN'-dinitramine (Bibl.112, 113). Inasmuch as technical ethylenediamine is obtained in the form of a 60 - 65% aqueous solution, direct nitration thereof by the action of nitric acid leads solely to the formation of a chemically
292 unstable salt readily soluble in water. Therefore, ethylene-NN'-dinitramine is obtained by nitration of the acyl or formyl derivatives of ethylenediamine.

In the USA, this product was obtained in a two-stage process industrially (Bibl.109, 114). The essence of each of the two stages is the following: in stage one, the mixture of aqueous ethylenediamine and diethyl carbonate solution was heated in an autoclave for 4 - 5 hrs at 170 - 190°. The process results in the formation of ethylene urea:

$$\begin{matrix}CH_2\cdot NH_2\\ |\\ CH_2\cdot NH_2\end{matrix} + \begin{matrix}C_2H_5-O\\ \diagdown\\ CO\\ \diagup\\ C_2H_5-O\end{matrix} \xrightarrow{-2C_2H_5OH} \begin{matrix}CH_2-NH\\ |\\ CH_2-NH\end{matrix} CO.$$

Water, alcohol, and excess unreacted substances are driven off, and the ethylene urea, obtained in the molten state, is discharged into a drip pan and, after solidification, either crushed to small pieces, or granulated, toward which end the melt is not allowed to solidify, but is run into cold water. The ethylene urea thus obtained has a melting point of 132 - 132.5°, and its yield is about 60% of theoretical.

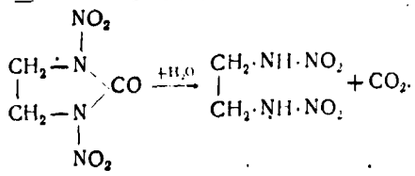
292 In the second stage, the ethylene urea is nitrated at 10° by a mixture of nitric and sulfuric acid consisting of 74% H_2SO_4, 15.4% HNO_3 and 10.6% H_2O (Bibl.109, 115). Subsequently, the mixed acid was replaced by 98% HNO_3 (Bibl.109):



The solution obtained is run into ice water. Crystals of NN'-dinitroethylene urea come down. Due to hydrolysis, precipitation is incomplete. The crystals are filtered off and washed, first in cold and then in warm water (50°).

In the laboratory, nitration is performed more conveniently with nitric anhydride in inert solvent (chloroform) at a temperature of 20 - 30°. The reaction goes rapidly and almost quantitatively. The reaction product is not soluble in chloroform and comes out of solution as it forms. The yield is about 90% of theoretical.

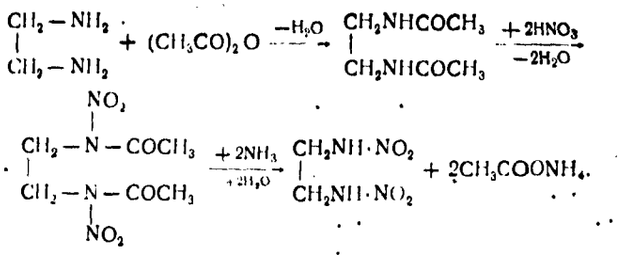
NN'-Dinitroethyleneurea is a crystalline product with a melting point of 211—212°. When boiled with water, it decomposes into CO_2 and ethylene-NN'-dinitramine:



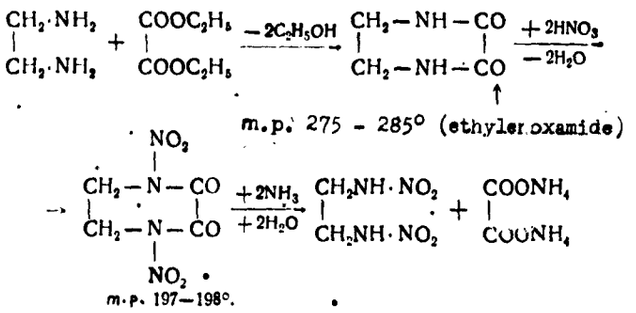
Because of significant shortcomings in the method described (low yield of the intermediate product — ethyleneurea, and the need to run a long reaction under pressure), a large number of researchers in the USA engaged in a search for other ways of producing ethylene-NN'-dinitramine. The most interesting of these methods is the following:

292 An aqueous solution of ethyelenediamine ~~XX~~ is heated with acetic ~~XXX~~ anhydride. Three or four moles of acetic anhydride are taken per mole of ethylenediamine. Acetic anhydride also serves as a dehydrator. The acyl derivative obtained is nitrated with

293 98% nitric acid in the presence of acetic anyhydride at a temperature of 0 - 5°C. At the conclusion of nitration, the nitromass is diluted with water to a concentration of 30 - 40% in terms of acetic acid. The crystals that come down as this occurs are filtered off and washed with cold water:



The nitration product is subjected to hydrolysis at room temperature by the action of 11-- 15% NH_3 solution. The low stability of ethylenediamine significantly reduces the advantages of this method. Replacement of ethylenediamine by ethyleneoxamide renders the method more advanced, inasmuch as the latter has greater stability.(it does not decompose upon nitration with 98% nitric acid or mixed sulfuric and nitric acid) (Bibl.112, 115). The chemistry of the product is as follows:



293 In the course of improving the production of ethylene-NN'-dinitramine, a cheaper method was developed, in the USA, for producing ethylenediamine from formaldehyde and hydrogen cyanide in accordance with the mechanism

$$CH_2O + HCN \rightarrow HOCH_2CN \xrightarrow[-H_2O]{+NH_3} H_2NCH_2CN \xrightarrow{2H_2} H_2NCH_2CH_2NH_2.$$

and nitration of ethyleneurea began to be performed with concentrated nitric acid.

Ethylene-NN'-dinitramine was obtained ~~XX~~ on apparatus for the production of tetryl, and the yield of ethylene-NN'-dinitramine was three times greater, and the cost considerably less than the cost of tetryl (Bibl.109).

Section 2. Nitroguanidine (Bibl.116)

Nitroguanidine was first obtained in 1877 by the action of concentrated nitric or sulfuric acid on ~~XX~~ guanidine nitrate. In industry, it is obtained by dehydration of guanidine nitrate by sulfuric acid.

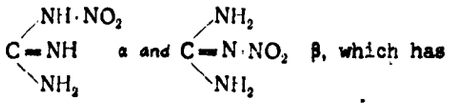
294 Despite the comparatively high explosive characteristics it displays, nitroguanidine is not used as an explosive by itself. During World War II, it was used as a component of nitroglycerine and nitrodiglycol powder instead of dinitrotoluene. There are many proposals for the utilization of nitroguanidine as a component of explosives.

Nitroguanidine apparently has a big future, inasmuch as its production is based on cheap raw materials: lime, coke, nitrogen from the air, ammonium nitrate, and sulfuric acid. Moreover, its production is related to that of a fertilizer - calcium cyanamide, from which guanidine nitrate, which is the starting product for the production of nitroguanidine, is obtained.(Bibl.117).

Nitroguanidine is the starting product for the production of tetrasene which is an

294 initiating explosive.

Nitroguanidine exists in two tautomeric crystalline forms (Bibl.118)



identical melting points of the order of 232 - 250° (melting with decomposition).

The α-form is obtained by the usual method of dehydration of guanidine nitrate: the action of sulfuric acid followed by decantation in water. This causes the product to crystallize out of the water in the α-form (long elastic needles that remind one of loosened asbestos).

The β-form is obtained in part upon dehydration of guanidine nitrate in the presence of ammonium sulfate. These forms are separated by means of a difference in their solubility in water. In the range of 25 - 100°, the β-form is more soluble than the α-, and at temperatures of less than 25° and more than 100°, the α-form is more soluble. Crystals of the β-form, recrystallized from water, are plate shaped. If crystals of the β-form are dissolved in sulfuric acid, and the solution is decanted into water, crystals of the α-form (Bibl.119) are obtained.

The specific gravity of nitroguanidine is 1.72.

Its solubility in water, organic solvents, sulfuric, and nitric acid is illustrated in Tables 93 - 95.

294

Table 93

a)	b)
Ether	0,04
Ethyl alcohol	0,18
Acetone	0,19
Methyl alcohol	0,50
Pyridine	1,75
Water	0,27
"	1,18 at 50°
"	10,36 at 100°

a) Solvent; b) Solubility, gm, at 20°, of Nitroguanidine (in 100 gm solvent)

Table 94

a)	b)
5	0,6
10	1,6
20	3,0
50	5,8
87	22,3

a) Concentration of HNO_3, %; b) Nitroguanidine solubility at 20°, gm (in 100 gm acid)

295 The best solvent for crystallization of nitroguanidine is water, but the crystals that come down are fine and are of very low gravimetric density (0.2 - 0.3). The gravimetric density of crystals is increased by adding colloidal substances (polyvinyl alcohol, gelatin, etc.) or substances that neutralize salts (urea nitrate, ammonium sulfate, etc.) to the solution.

Table 95

a)	b)	
	0	25
45	5,8	10,9
40	3,4	8,0
35	2,0	5,2
30	1,3	2,9
25	0,7	1,8
20	0,4	1,0
15	0,3	0,5

a) Concentration of H_2SO_4, %;
b) Nitroguanidine solubility, gm, at temperature, °C (in 100 cc acid)

Depending upon the conditions of crystallization, the gravimetric density fluctuates from 0.2 - 0.8.

Nitroguanidine forms eutectic mixtures (Bibl.115), shown in Table 96, with a number of substances.

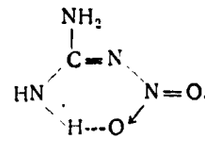
295

Table 96

a)	b)	c)
NH_4NO_3	20	131,5
Guanidine nitrate	41	166,5
17.5% guanidine nitrate and 25.5% NH_4NO_3	57	113,2

a) Component; b) Amount of nitroguanidine in eutectic, %; c) Melting point of eutectic, °C

The following is the structural formula of nitroguanidine (Bibl.120, 121, 122, 123):



Nitroguanidine XI has weakly basic properties. Under normal conditions it is a stable compound. In hot water it hydrolizes in part:

$$NH_2-\underset{\underset{NH}{\|}}{C}-NHNO_2 \rightarrow NH_3+NO_2HN-CN \quad \text{(nitrocyanamide)},$$

and, upon boiling, hydrolysis goes very intensively to formation of gaseous products:

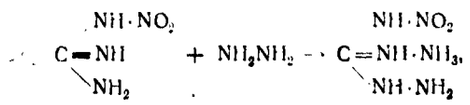
$$NH_2-\underset{\underset{NH}{\|}}{C}-NHNO_2 \xrightarrow{+H_2O} 2NH_3+N_2O+CO_2.$$

296 Weight losses of nitroguanidine, when its solutions are heated in an autoclave at 120° for 48 hrs, are (in %):

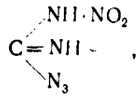
in acid medium (pH = 3.9 - 6)	0.19
in neutral medium (pH - 7 ÷ 9)	0.51
in alkaline medium (pH = 8 - 9)	2.74

296 (the change in pH in the course of heating is shown in parentheses). As these data indicate, nitroguanidine is more stable in an acid medium.

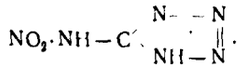
Nitroguanidine results in an explosive substance in an aqueous hydrazine solution (the substance has a melting point of 182°):



which converts to nitroguanidine azide under the action of hydrazoic acid (at 0°)

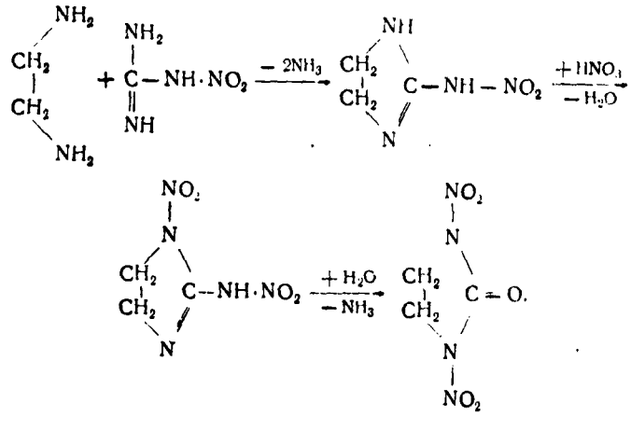


while at 70° it converts to nitroaminotetrazole



Both these substances are initiating explosives.

Reacted with ethylenediamine, nitroguanidine yields cyclic derivatives:



The explosive properties of nitroguanidine are: fugacity 290 - 300 cc, brisance 16.5 mm, velocity of detonation 7920 m/sec at Δ = 1.56 and 8440 m/sec at Δ = 1.64.

297 Shock sensitivity and friction sensitivity are considerably less than that of TNT (Bibl.124, 125).

Methods of production. A number of methods of producing nitroguanidine (Bibl.126, 127, 128) are known. However, in industry, it is produced by dehydration of guanidine nitrate by sulfuric acid (Bibl.129, 130):

$$\begin{matrix} NH_2\cdot HNO_3 \\ C=NH \\ NH_2 \end{matrix} \xrightarrow[-H_2O]{+H_2SO_4} \begin{matrix} NH\cdot NO_2 \\ C=NH \\ NH_2 \end{matrix}$$

The process is 95% sulfuric acid, 2.5 parts thereof (by weight) being used per part of nitrate. The use of less concentrated acid or a smaller quantity thereof reduces the nitroguanidine yield. H_2SO_4 stronger than 95% decomposes the nitroguanidine. The optimum process temperature is 30°, and reaction time is 10 min. At higher temperature or longer reaction time, the finished product will undergo partial decomposition. Nitroguanidine is isolated from the reaction mixture by dilution with spent sulfuric acid to 18 ÷ 20% concentration.

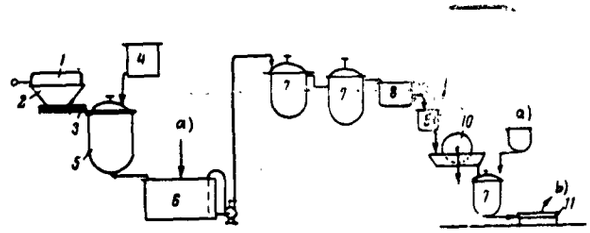


Fig.90 - Diagram of Nitroguanidine Production

1 - Sieve; 2 - Bunker; 3 - Screw conveyor; 4 - Acid metering tank; 5 - Dehydrator (nitrator); 6 - Diluting tank; 7 - Crystallizers; 8 - Condenser; 9 - Feed tank; 10 - Vacuum filter; 11 - Filter hopper a) Water; b) To drying

The guanidine nitrate entering the production process is tested in the laboratory by experimental dehydration. With continuous agitation of the nitro mass, 125 gm of 95% H_2SO_4 is run into a beaker and 50 gm guanidine nitrate is introduced at 30° in 10 min. The process should go smoothly without temperature jumps or emission of white fumes. At the end of the period of agitation, the mass is held at 30° for another 30 min, then cooled to 0 - 5° and decanted into precooled water (500 cc). Then the nitroguanidine is filtered on a Schott filter, washed with cold water, and dried XX for 10 hrs at X 60°.

Figure 90 presents a schematic diagram of the production of nitroguanidine.

Dry guanidine nitrate is delivered from the rocking sieve to a bunker, from which it goes XXXXXXXX by screw conveyor to a dehydrator filled with 96 - 98% H_2SO_4. Sulfuric acid, 2.5 parts by weight per part of guanidine nitrate, is employed. The reaction is run XXXXX at 30 - 35° for 10 min, whereupon the mixture is discharged into a dilution tank filled with cold water. The diluted mass is sent by centrifugal pump to the first crystallizer, XXXX from which it flows into the second. From the second crystallizer, the mass, having undergone further cooling in a condenser, goes to a drum vacuum filter, from which it is sent to a crystallizer filled with cold water.

Recrystallization is performed as follows. To the hot solution (95 - 98°), consisting of 300 kg nitroguanidine diluted by 6 m^3 of water, 7.5 kg ammonium nitrate
298 and 3 kg glue are added. The solution is cooled slowly, with intense agitation, over the period of an hour, to 15 - 16°. The nitroguanidine crystallizes as a rather XXXX dense deposit (Δ = 0.8) which is squeezed out on a filter and dried in a pneumatic desiccator.

During World War II, nitroguanidine production in Germany attained some 3,000 tons

298 per month. The consumption of raw materials was 1.36 tons guanidine nitrate and 3.0 tons 98% sulfuric acid per ton.

Section 3. Diethanol-N-nitraminedinitrate (DINA)

Diethanol-N-nitraminedinitrate or DINA

$$NO_2-N\begin{matrix}CH_2CH_2ONO_2\\CH_2CH_2ONO_2\end{matrix}$$

was first obtained in 1942 by Wright (Bibl.131) who, during the subsequent years, significantly improved the initial method of production and found a catalyst for the N-nitration process. DINA approximates hexogen in its explosive properties.

In 1944, the USA began to produce this product at a small installation. Considerable expansion of the production of DINA was envisaged, and the utilization of hexogen equipment toward this end was planned (Bibl.109).

DINA was employed to fill detonators for naval guns. Its use for other purposes was found impossible due to its inadequate stability, high shock sensitivity, and low melting point.

DINA is a crystalline product. Its specific gravity is $d_{4^\circ}^{15^\circ}$ = 1.67, and its gravimetric density is 0.8 - 0.9, melting point 49.5 - 51.5°, heat of fusion 23.5 kcal/kg, specific heat 0.38 kcal/kg/°C. The product is not hygroscopic and not volatile.

Concentrated sulfuric acid decomposes DINA even at 0°. A 10% alkaline solution induces decomposition, but at considerably slower rate.

In the dry condition, the pure product is of adequate stability, but in an aqueous medium, and particularly in boiling water, DINA decomposes slowly (attaining approximately 30% decomposition in 6 hrs).

298 As distinct from PTEN and hexogen, DINA is a good plasticizer for nitrocellulose and may be used to substitute for nitroglycerin in powders.

The explosive properties of DINA are: heat of explosive decomposition 1250 kcal/kg, velocity of detonation 7350 m/sec (at Δ = 1.47). Shock and friction sensitivity are somewhat less than those of PTEN, but greater than that of hexogen.

DINA is obtained (Bibl.132, 133) by nitration of diethanolamine, and the initial diethanolamine is obtained by condensation of ethylene oxide with ammonia in accordance with the following scheme

$$\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}\!\!>\!O + NH_3 \rightarrow \begin{matrix} NH(CH_2 \cdot CH_2 \cdot OH)_2 \\ NH_2CH_2CH_2OH \\ N(CH_2CH_2OH)_3 \end{matrix} \xrightarrow{dist.} \rightarrow NH(CH_2CH_2OH)_2$$

Condensation is run at 60° under pressure. Three products result: mono-, di-, and triethanolamine, as a consequence of which the yield of the desired product is low. The presence of mono- and triethanolamines in the nitration of diethanolamine is

299 undesirable due to the formation of unstable products from these. The isolation and purification of diethanolamine is by vacuum distillation, the fraction boiling between 145 - 155° at a residual pressure of 10 mm Hg being taken off.

The usual type of nitration of diethanolamine results in the formation of diethanolamine dinitrate, but nitration in the presence of a chlorine ion as promoter leads to the formation of DINA. The catalytic action of the chlorine ion on the process of the formation of N-nitramines from secondary amines was discovered by Wright and employed by him to synthesize DINA (Bibl.131, 132, 134).

Nitration of diethanol to DINA is performed by 98% nitric acid (not containing nitrogen oxides) at 20 - 30° in the presence of acetic anhydride and hydrogen chloride

catalyst.
299 as a promoter. Hydrogen chloride may be replaced by a salt such as zinc chloride. In the presence of a catalyst, product yield is about 90%, but without one the yield is low. The process goes in accordance with the following equation

$$HN(CH_2CH_2OH)_2 + 3HNO_3 \xrightarrow{3(CH_3CO)_2O} NO_2 \cdot N(CH_2CH_2ONO_2)_2 + 6CH_3COOH.$$

In the presence of a catalyst, the hydrogen of the amino group is not replaced by the nitro group, but formation of the nitrate salt occurs instead:

$$HN(CH_2CH_2OH)_2 + 3HNO_3 \rightarrow HNO_3 \cdot HN(CH_2CH_2ONO_2)_2 + 2H_2O.$$

The salt obtained is a crystalline substance with a melting point of 125°. It is unstable, readily loses the HNO_3, is highly hygroscopic, and readily soluble in water.

If nitration be run with nitric acid containing nitrogen oxides, diethanol-N-nitrosoaminedinitrate is formed in accordance with the equation

$$HN(CH_2CH_2OH)_2 + 2HNO_3 + HNO_2 \rightarrow NO \cdot N(CH_2CH_2ONO_2)_2 + 3H_2O.$$

The nitroso compound formed is unstable and is readily decomposed with formation of nitrogen oxides which, in turn, decompose the basic product. The nitroso derivatives may be converted to DINA by oxidation of the NO group to NO_2 by, for example, potassium persulfate.

Technological process for production of DINA. The first stage in the process is nitration, which is performed in a nitrator. Acetic anhydride is run into the nitrator, and HNO_3 and diethanolamine are added to it with agitation. Ten percent more HNO_3 than

catalyst

299 the theoretically required amount is XX employed. A promoter in the form of saturated HCl solution in diethanolamine is introduced, 0.02 mole per 1 mole diethanolamine, into the acetic anhydride at the beginning of the process. Fifteen moles acetic anhydride are employed per mole diethanolamine. The components are run in at 5 - 10°, and the mixture is then held for 10 min at 40°. At the conclusion of the process, and in order to reduce corrosion of the apparatus, the reaction mixture is blown free of the nitroso chloride. Then, the mixture is discharged from the nitrator into a tank of cold water, to reduce the concentration of the spent acid to 30%. A portion of the impurities go into solution as this XXX occurs. The resultant crystals are filtered,

300 washed with water and NaOH solution to a pH of 5.6 to 6.3. The filtered product is transferred to boiling water and, for 15 min,, treated with live steam.

If the initial diethanolamine is of low quality, then a solution of sodium bicarbonate is employed instead of water, and treated with live steam for 8 min, whereup acetic acid is added to neutral reaction and again treated with live steam for another 7 min. The molten DINA is XXXX separated from the hot aqueous layer and decanted into acetone, enough of which is used to assure complete solution. The warm acetone solution is diluted, in an aluminum vessel, with an agitator, by twice the volume of water, containing 0.25% ammonia, and permitted to cool to 20 - 25°, with unceasing agitation. Crystallization of DINA occurs in this process.